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MEASUREMENT OF COAL WETTABILITY
AND PREDICTION OF THE HYDROPHOBIC
NATURE OF OXIDIZED COAL

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OF OXIDIZED COAL"

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Dear Nels:

Enclosed are the ten copies of the report on coal wettability and flotability. I am greatly appreciative of your contribution and support.

In order to present a comprehensive picture of the topic I took the liberty of including some of the findings obtained under the support of other funding agencies. I hope that you will find the report to your satisfaction.

In the beginning of spring I will be sending you a literature review dealing with the beneficiation of difficult-to-float coals and I hope that my graduate student will soon be finished with his review of the use of flotation in the processing of dispersed energy resources. I would greatly appreciate your comments on both.

Looking forward to meeting you during my visit to Alberta.

Yours sincerely,

A handwritten signature in dark ink, appearing to read 'A. M. Al Taweel', with a stylized flourish at the end.

A. M. Al Taweel
Professor

AMAT/cjr
Encl.

MEASUREMENT OF COAL WETTABILITY
AND PREDICTION OF THE HYDROPHOBIC NATURE
OF OXIDIZED COAL

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I INTRODUCTION

Wetting characteristics of coal play an important role in determining the effectiveness of several coal beneficiation processes such as agglomeration, flocculation and flotation [1-3]. These selective separation approaches utilize the difference in surface properties between the predominantly hydrophobic organic component, and the undesirable hydrophillic inorganic components, in order to separate the latter. Knowledge of the surface characteristics of each component is, therefore, essential for the selection of appropriate processing conditions.

Satisfactory suppression of coal dust by means of water spraying is also influenced by the surface characteristics of coal, which are often rendered more hydrophillic through the addition of surfactants to the water spray and their subsequent adsorption on the surface of coal. On the other hand, the flotation characteristics of oxidized coals can often be improved through the adsorption of appropriate reagents which can improve the surface's hydrophobicity [6]. The maximum solid loading achievable in coal/water slurries, as well as their stability and rheology, was also found to be strongly influenced by the surface characteristics of coal [7,8].

A number of techniques for measuring coal wettability have been used, including methods based on infusion [4,9,10], contact angle measurement on polished surfaces [11-15], minimum pressure needed for bubble formation [16], differential flotability [17], as well as by the imbibition within an advancing freezing front [18-19]. Indirect methods for measuring surface energy

were also used with the heat of wetting [20-22] and the free energy of adsorption [23] being the most commonly used techniques.

Because of its simplicity, the extremely simple test developed by Walker et al. [24], namely the wetting time, was extensively used to investigate the surface properties of coal. Thus, Papić and McIntyre used it for investigating the effect of surfactants on coal [25] while Doeksen [26] used it to evaluate various methods of coating coal. Glanville and Wightman also used this technique to study the role of dispositive ions in the wetting of coal by anionic surfactants [5] and to determine the critical surface tension of coal [27]. A comparison between this test and the Draves test found that they are well correlated over a wide range of surfactant concentration and structure [28].

Unfortunately, the results obtained using different techniques are not always in agreement and a research program was, therefore, initiated to compare between the various techniques and evaluate their sensitivity to variation in the surface characteristics of coal powders. Seven different techniques were evaluated using coal oxidized to various levels and were compared as to their reproducibility, sensitivity as well as to their cost and ease of operation. These techniques are:

- 1) wetting time
- 2) contact angle of flat wetted bed of compacted powders
- 3) capillary pressure during liquid imbibition in a powder bed
- 4) dynamic penetration of liquid through a powder bed

- 5) minimum pressure needed for the formation of a bubble under a wetted bed.
- 6) heat of wetting
- 7) adsorption isotherms.

Another objective of this research program is the determination of the impact of the coal's surface characteristics on its flotability, and the selection of the wettability measuring technique most suitable for predicting the recoveries achievable. Finally, a number of surface conditioners for restoring the hydrophobicity of coal were tested and evaluated with regard to their ability to enhance coal recoveries by flotation.

EXPERIMENTAL

II.1 Techniques

Wetting time experiments were conducted in glass cylinders placed in a thermostatically controlled bath at $25 \pm 0.2^\circ\text{C}$. A wide range of experimental conditions were investigated.

Sample weight	0.05 - 0.3 g
Liquid surface area	7.6 - 33.1 cm ²
Particle size	25 - 18.0 mm

In addition to using aqueous methanol solutions of varying concentration, a whole series of organic liquids were also tested (Table 1).

Trials with the H-E method [29,30], have been undertaken in order to test its usefulness for evaluating the wettability of coal particles. Pellets of coal (2.54 cm in diameter) were prepared using several narrowly sized coal fractions as well as admixture of two sizes. Compaction pressures of up to 50,000 psi (4450 MPa) were applied and the experimental conditions investigated in the preliminary set of experiments are outlined in Table 2.

Reasonably good pellets were formed under these pressures; however, liquids placed on their surfaces were imbibed by the pellets rather than forming distinguishable drops on the surface. The imbibition time of water droplets (0.015 ml) deposited on the pellets was, therefore, measured for coal pellets prepared under compressive pressures of 9,000 MPa.

TABLE 1 Liquids Used In Evaluating Wetting Time of Coal

Alcohols	γ_{LV}	Mono Substituted Benzene Derivatives		Other Aromatic Compounds		Aqueous Ethanol Solutions Concentration	
		γ_{LV}		γ_{LV}		wt %	
Methanol	22.1	Benzene Toluene Chlorobenzene Bromobenzene Benzonitrile Nitrobenzene Aniline	27.9 28.1 32.5 34.9 38.3 42.6 42.7	P-xylene m-xylene o-xylene Acetophenone o-Toluidine Benzyl alcohol	28.1 28.3 28.7 37.5 39.5 39.6	90.1% 73.5% 51.9% 32.9% 27.3% 21.4% 19.1% 18.1% 10.1%	23.3 24.8 27.0 31.2 32.9 36.2 37.6 38.7 46.5
Ethanol	21.9						
Propanol	23.4						
n-Butanol	24.0						
n-Pentanol	24.8						
n-Hexanol	26.5						
n-Heptanol	26.3						
n-Octanol	27.0						
n-Decanol	27.9						

γ_{LV} Surface tension, MN/M

Table 2 Preliminary H-E Testing Conditions

Particle Size (CSA Tyler)	Compaction Pressure psi	Liquids Tested
-60 + 100	3000 4000	C Cl ₄ Hexyl Alcohol
-100 + 200	2000 4000	Water Formamide
50% -60 + 100	4000	Ethylene Glycol
50% -100 + 200		
-200 + 270	50000 100000	Water

The capillary pressure resulting from the imbibition of liquid in a bed of powdered coal has been measured using the technique proposed by Sell [31,32]. It relies on the measurement of the air pressure required to prevent further penetration of the wetting liquid into a vertical bed of compacted solids. In order to attain a reproducible capillary structure, coal samples were compacted using a procedure similar to ASTM standard No. D4164-82. The capillary pressure resulting from the imbibition of 25% aqueous Methanol were monitored using pressure transducers.

The rate of weight gain resulting from liquid imbibition in a compacted bed of coal was also monitored in order to determine its surface characteristics [32]. In a manner similar to capillary-pressure measurement, it was necessary to use a standardized compaction technique in order to achieve a high degree of reproducibility.

Another indication of the capillary pressure can be obtained by measuring the minimum pressure needed for the formation of a bubble under a wetted bed [16]. This technique, however, differs from the previously mentioned method by its dependence on the receding angle of contact. Dry nitrogen gas was used to minimize surface alterations and the pressure was detected using a U-tube manometer.

The heat of wetting was measured in a microcalorimeter in which temperature measurement accuracy of $\pm 0.005^\circ\text{C}$ was achieved. The calorimeter constant depended on the liquid tested, and varied between 170-410 cal/g $^\circ\text{C}$.

The adsorption characteristics of methanol, benzene, n-heptane and water vapours on various coal samples was determined using the dynamic adsorption technique. The apparatus used for this purpose consists of a gas chromatograph (Perkin Elmer SIGMA 115) to which a small saturator filled with the desired adsorbate is connected. Coal samples were packed inside a 6 mm i.d. glass column which was used in the chromatograph. The response to a step change in adsorbate concentration (adsorption and desorption) was monitored and analysed in accordance with Glueckauf's method [33]. The BET surface areas were obtained from the equilibrium isotherm data using standard methods [34].

Flotation tests were conducted using the cell proposed by Siwek et al. [35]. This design was selected in preference to the more conventional Hallimond tube in order to minimize errors resulting from mechanical

entrainment within the fluid streams, a factor which is expected to play a large role in the case of coal ($\text{Sp.Gr} = 1.2\text{--}1.3$).

The experimental setup used is shown schematically in Figure 1. A known amount of the coal sample (approx. 2 gram) was conditioned outside the cell for a specified period after which the sample was transferred to the cell. Flotation tests were conducted in a 10 ppm MIBC/ $1\text{--}4\text{M}$ NaCl solution and the liquid level in the cell was selected to be high enough to have a continuous liquid bridge between the flotation and collection sections, thereby eliminating any contribution by the froth layer to the selectivity and recovery of the flotation test. Flotation characteristics will hence be mainly determined by collision frequency between bubbles and particles and the resistance of the aggregate formed to rupture by hydrodynamic forces.

In order to select appropriate hydrodynamic conditions within the cell, the interfacial area of contact was determined using a laser-based light attenuation technique [36] and the results obtained are shown in Figure 2. The interfacial area was generally found to be rather insensitive to variation in the speed of rotation, an observation which suggests that the bubble sizes are mainly controlled by the structure of the sintered glass distributor. On the other hand, the interfacial area was found to increase progressively with increasing gas flow rates with the incremental increase tending to flatten out at high gas flow rates due to the tendency of bubbles to coalesce. Tests were, therefore, conducted at a gas flowrate of 0.08 cm/s and a rotational speed of 380 rpm. Higher rotational speeds were found to move the coal

particles away from the path of the rising bubbles. Similarly, as can be seen from Figures 3 & 4, coal recovery after 10 minutes was found to increase slightly with increasing air flow rate, reaching a constant value for $VG > 0.05$ m/s.

The kinetics of coal flotation, and the reproducibility of the flotation test, was evaluated using a coal of relatively low natural flotability (Prince Mine Coal). For a flotation time of 10 minutes the reproducibility among repetitive tests was found to be $\pm 5\%$ and was, therefore, considered as the standard testing condition throughout the whole research program.

In addition to evaluating the natural flotability of coal, influence of the following surface conditioning parameters was investigated.

- Kerosene at various degrees of preemulsification.
- Dowell m210 various combinations with kerosene.
- Alchem 8E34
- Ethyl acetate.
- Heptanol.
- Hexadecyl pyridinium bromide.

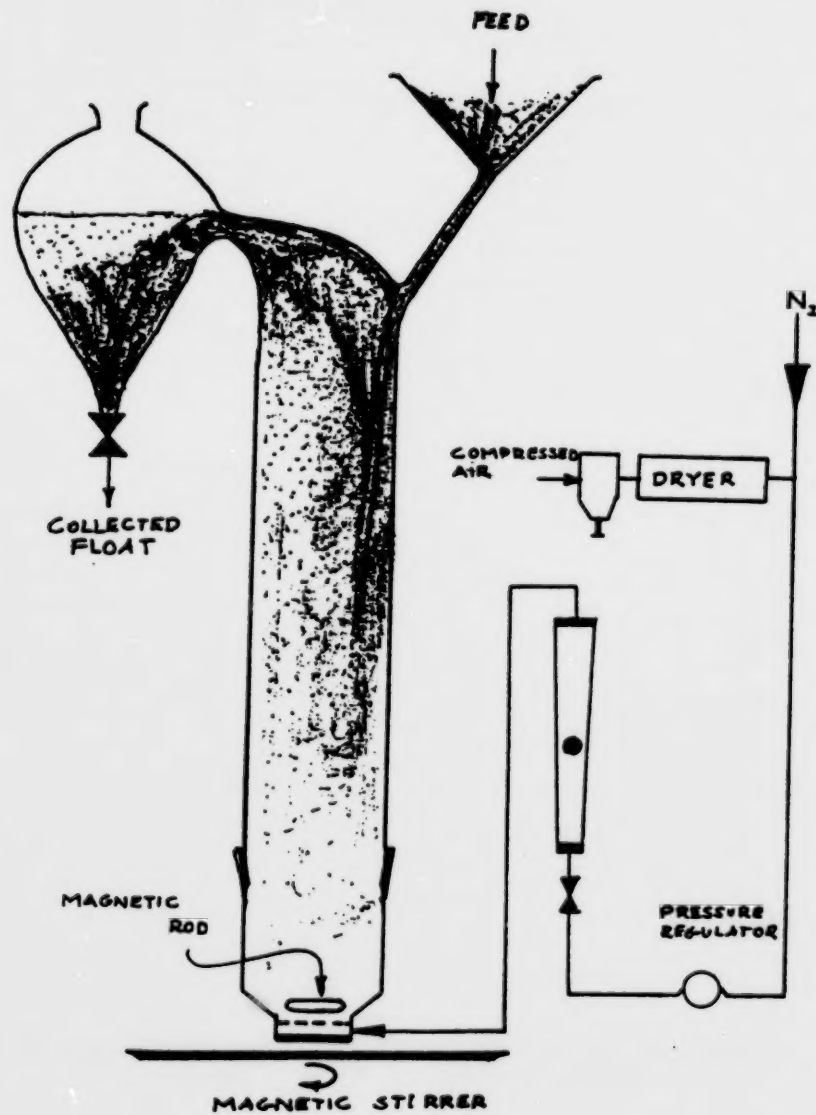


Figure 1: Cell Used In Evaluating the Flotability of Coal

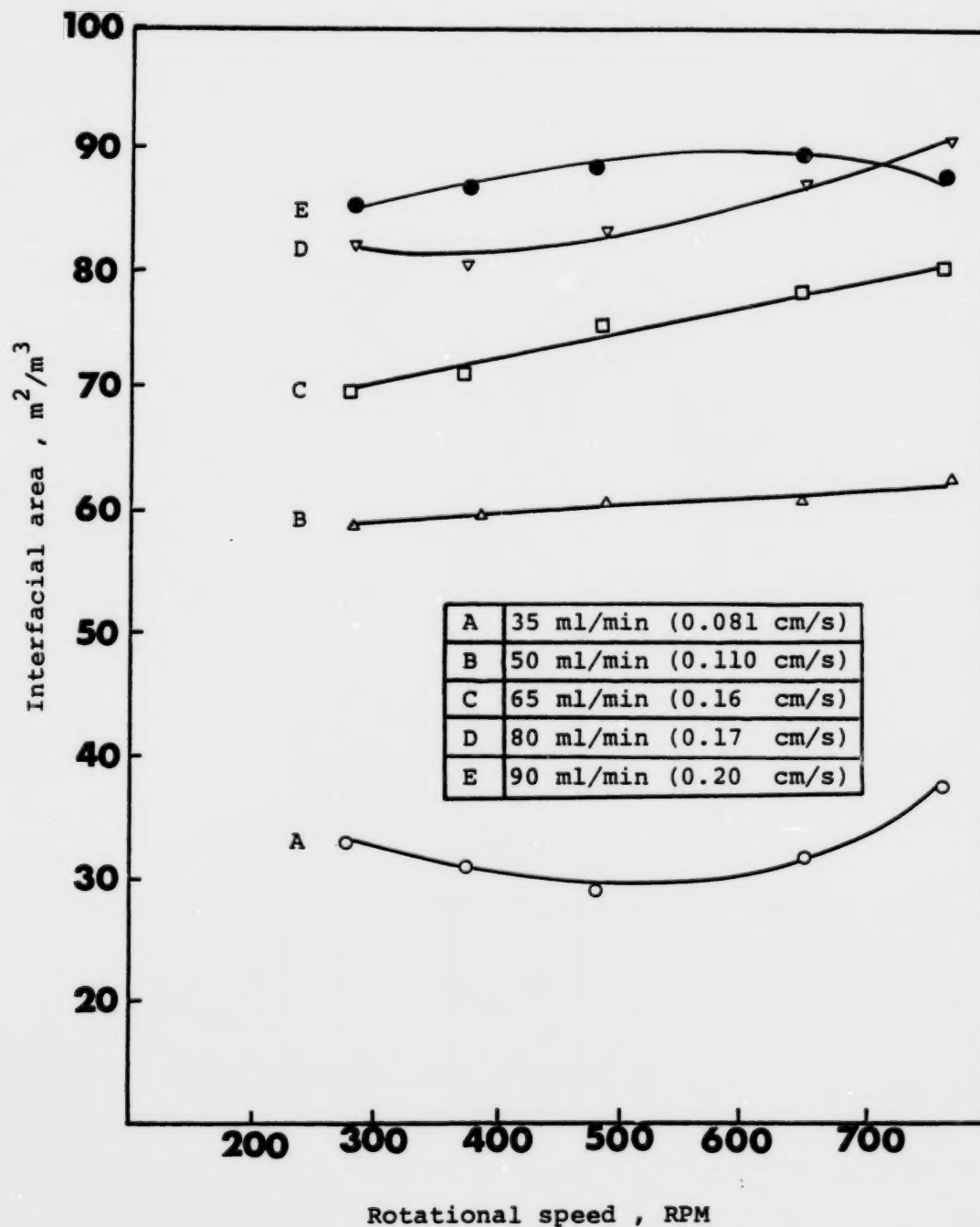


Figure 2: Hydrodynamic Characteristics of Gas/Liquid Contact in the Siwek Flotation Cell

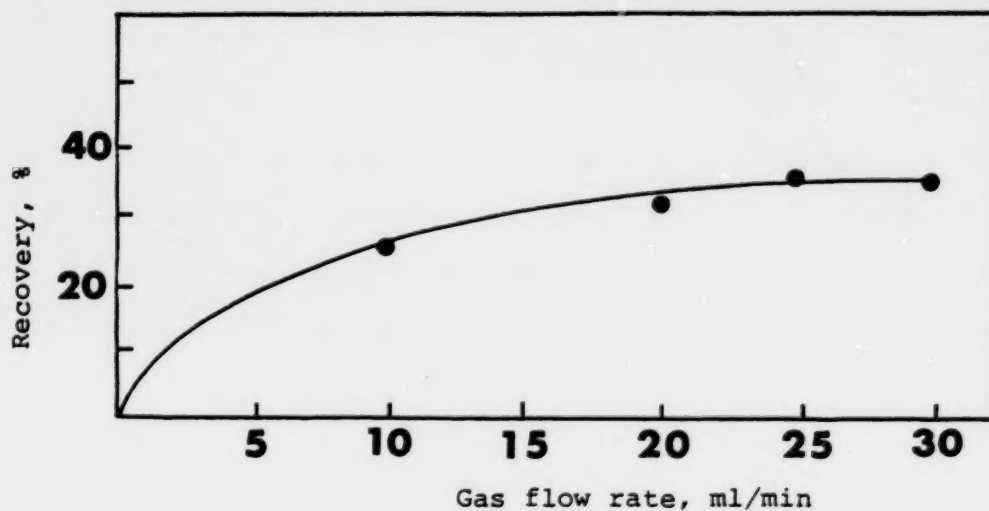


Figure 3: Effect of Gas Rate On the Recovery by Flotation After 10 Min.

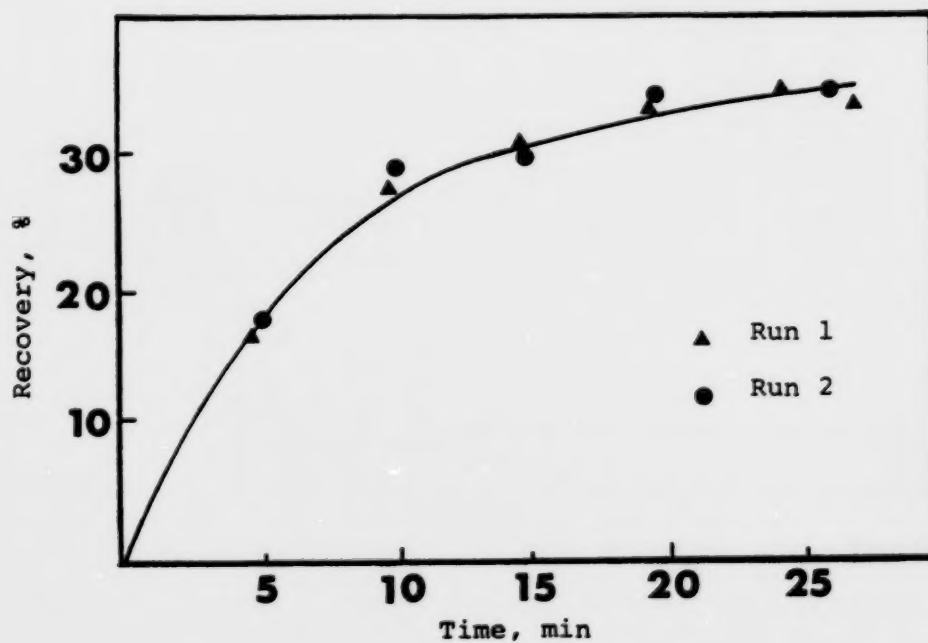


Figure 4: Kinetics of Coal Beneficiation By Flotation
(gas flow: 30 ml/min, 10 ppm MIBC and 10^{-4} molar solution of NaCl)

II.2 Materials

Eight coal samples varying in origin, rank and extent of weathering were tested in conjunction with a coal sample which has been artificially weathered at 7 different levels of oxidation. The samples were air dried, ground and sieved through 70, 100, 140, 200 and 270 mesh CSA sieves. The characteristics of these samples are summarized in Table 3 and Figures 5-9.

Table 3 Ultimate and Proximate Analysis of Coals Tested[†]

Sample	C	H	S	N	O*	Ash	Moisture	VM	FC
EMR 1	87.41	5.56	0.99	1.32	4.71	14.5	0.80	37.0	47.7
EMR 2	84.14	5.10	0.42	1.09	9.25	9.6	0.80	27.7	61.9
EMR 3	86.07	6.51	0.47	1.32	5.62	26.4	1.00	22.7	49.9
EMR 4	76.56	6.03	0.57	0.30	16.53	16.2	4.70	40.4	38.7
EMR 5	76.18	4.26	0.50	1.11	17.95	33.7	8.50	33.9	23.9
EMR 6	84.68	5.68	0.29	0.72	8.63	9.0	0.70	21.8	68.5
Prince	73.6	5.89	3.25	1.35	15.91	14.4	3.87	33.4	48.1
Devco No 26	87.1	5.70	0.80	1.40	5.00	3.1	2.14	34.8	59.4

[†]d.a.f. basis

-200 + 270 CSA Mesh

*by difference

Prince mine coal samples were artificially oxidized in a manner similar to that proposed by Wen [37] using dry air at 100°C flowing at the rate of 100 ml/min. Although this treatment resulted in significant alteration in the surface properties of the coal, it was found to exhibit no detectable difference in ultimate analysis.

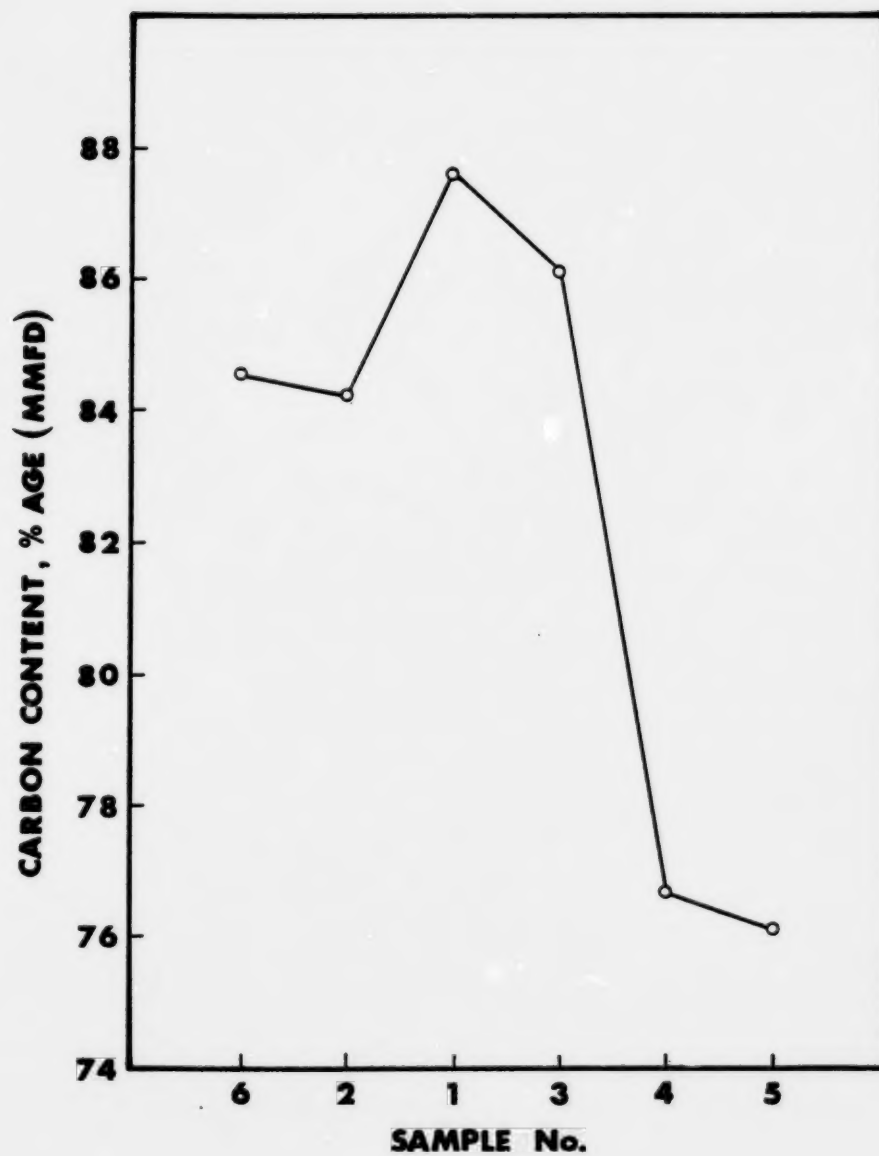


Figure 5: Carbon Content of Western Coal Samples

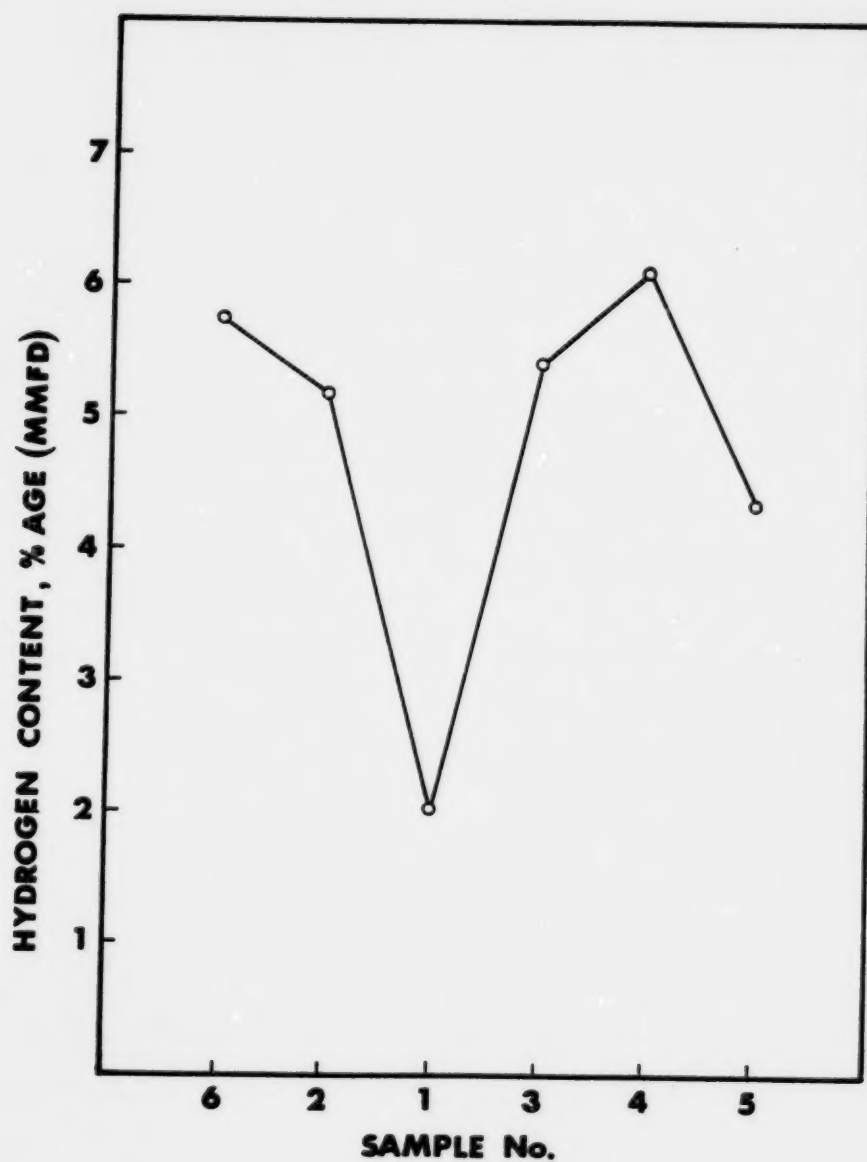


Figure 6: Hydrogen Content of Western Coal Samples

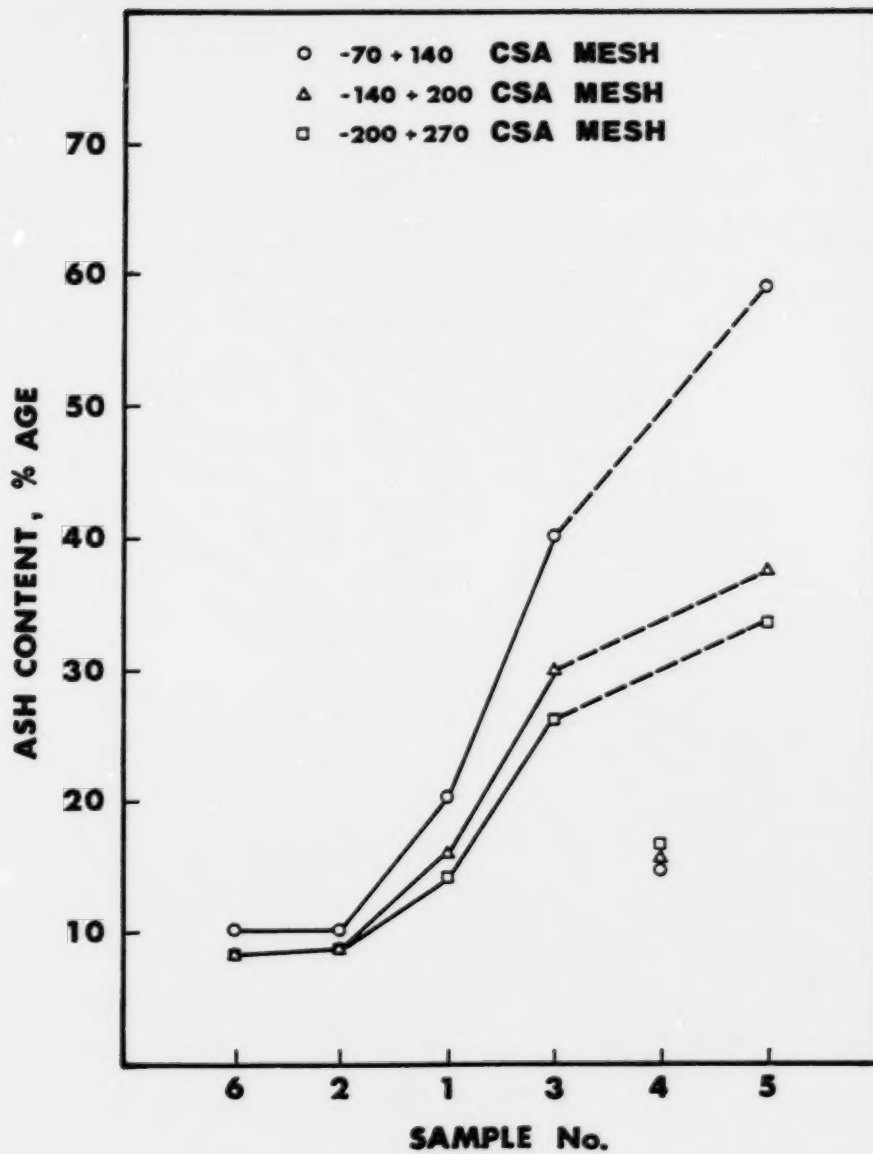


Figure 7: Ash Content of Western Coal Samples

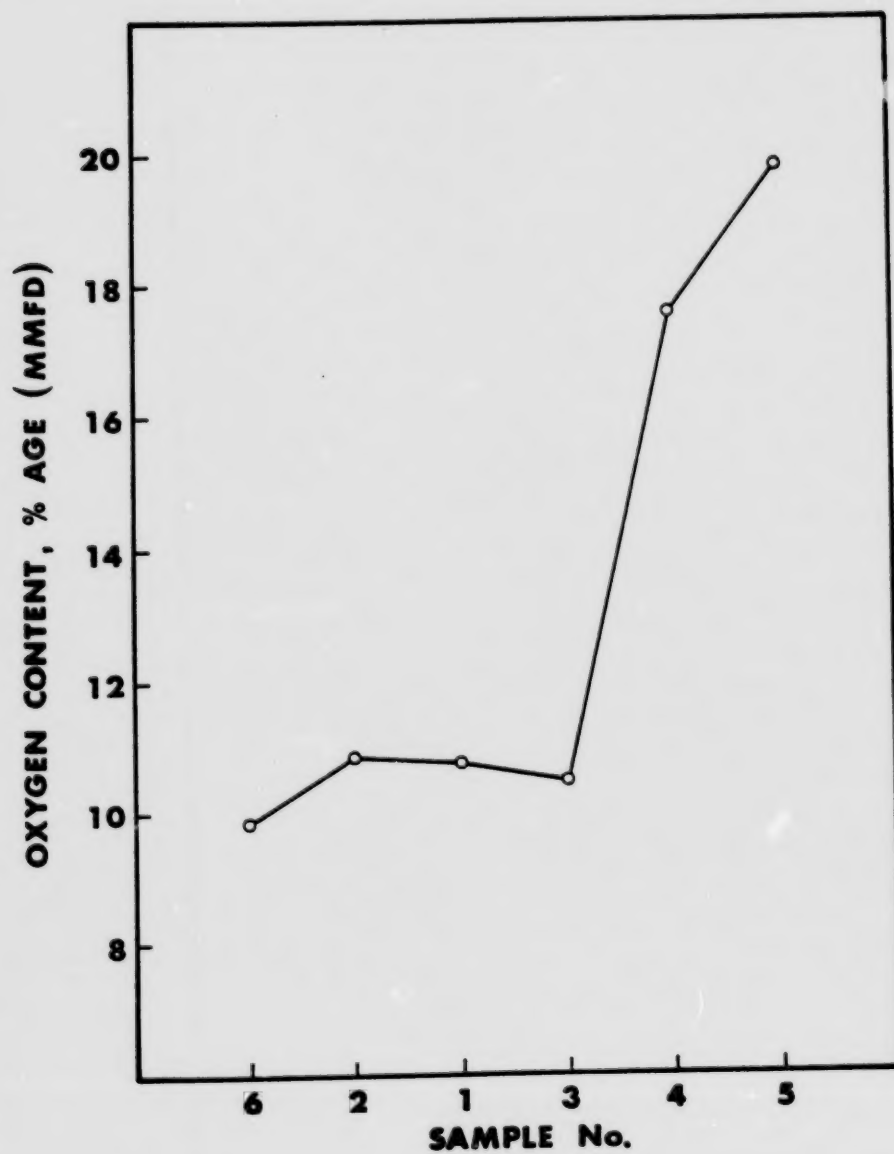


Figure 8: Oxygen Content of Western Coal Samples

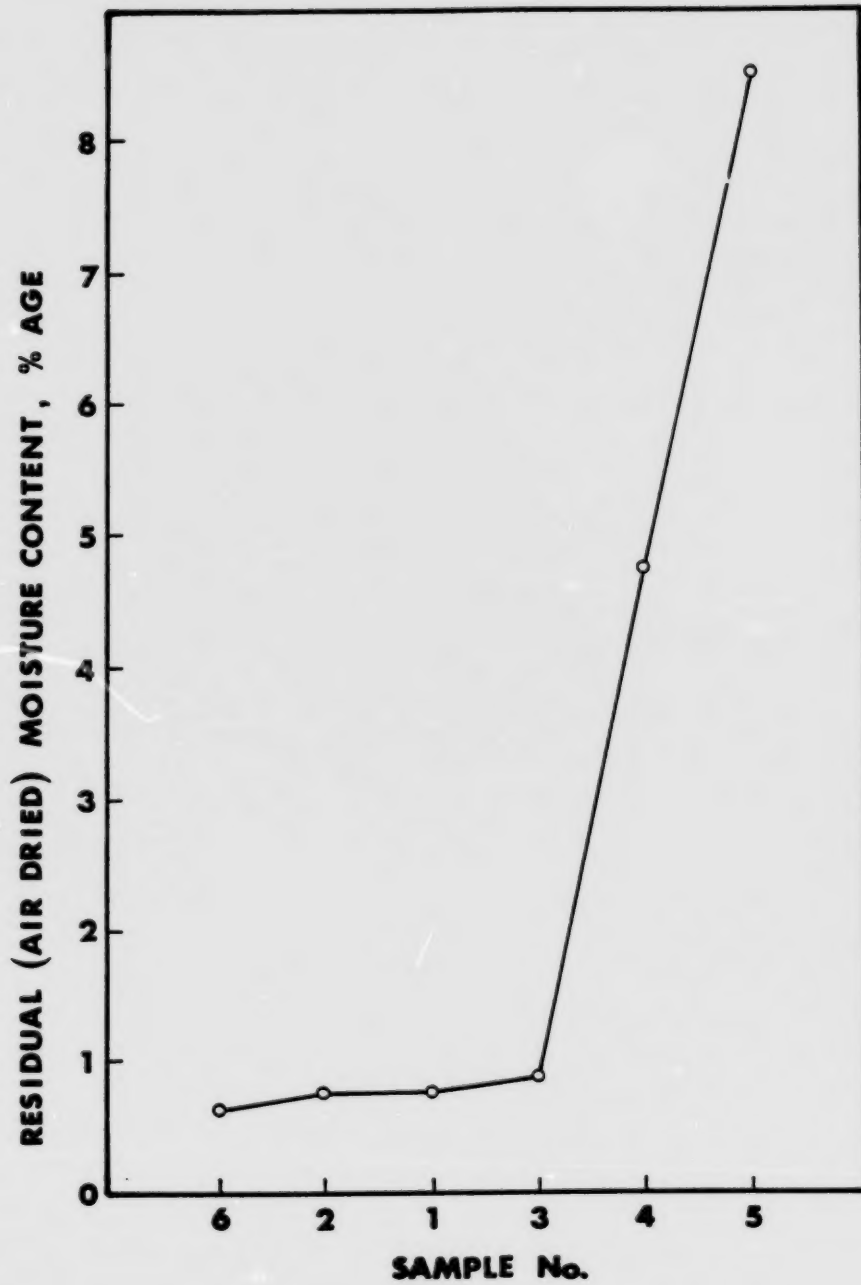


Figure 9: Residual Moisture Content of Western Coal Samples

Due to the high ash content in most of the samples investigated, and the possibility of selective grinding of coal and shale, the ash content in the different size fraction was evaluated and is summarized in Table 4.

Table 4 Ash Content In Different Fraction of Coals Tested

SAMPLE	FRACTION			
	-70+140	-140+200	-200+270	-270
EMR 1	20.4	16.2	14.4	13.2
EMR 2	10.6	9.6	9.6	9.1
EMR 3	39.8	30.2	26.4	27.8
EMR 4	14.6	15.7	16.2	17.4
EMR 5	58.4	37.7	33.7	32.3
EMR 6	10.5	9.2	9.1	9.0
Prince	11.25	12.5	14.6	27.1

Depending on their origin, coals were found to behave differently with respect to their response to grinding. The shales present in coals 5, 3 and 1 are presumably harder than the coal matrix, with the resulting decrease in ash content with decreasing particle size. On the other hand, the shales present in sample No. 4 appears to be softer than the organic matrix, whereas no significant stratification was observed with coals No. 2 and 6. The Prince mine coal depicts a rather unique characteristic, namely the tendency of its shale to crumble into fine particles which concentrate in the very fine fraction.

These large variations in ash content result in significant differences

in coal density, which in turn can have quite an impact on coal beneficiation processes. The density of various fractions from Prince mine coal was, therefore, measured and the density of the organic matrix computed assuming an average ash density of 2.7 g/cm. The results shown in Table 4 indicate that the density of the organic matrix is independent of the ash content present in the coal, and the small variation in matrix density ($\pm 0.7\%$) encouraged the computation of the effect of ash content on the density of various coals (Figure 10).

Table 5 The Ash Content In Different Fractions of Prince Mine Coal

Particle Size m mesh	Ash content (%)	Density of particle (g.cm ⁻³)	Corrected coal density* (g.cm ⁻³)
-270	27.1	1.431	1.218
-200 + 270	14.6	1.308	1.202
-140 + 200	12.5	1.316	1.226
-100 + 140	11.5	1.302	1.220
-70 + 100	11.0	1.294	1.216
			$x = 1.2164 \pm 0.008$

*Densities of organic phase as determined by displacement in methanol. Correction for mineral matter content was made assuming average ash density of 2.7 g.cm⁻³.

Artificially oxidized coal samples were prepared by batchwise oxidizing about 120 gm of coal in a manner similar to that used by Wen [37]. Pure dry oxygen at 100°C was passed through the sample (ml/min) for the duration of 14, 28, 49, 70, 84 and 120 hours in order to yield samples of progressively higher degrees of oxidation. As shown in table 6, this treatment resulted in minor

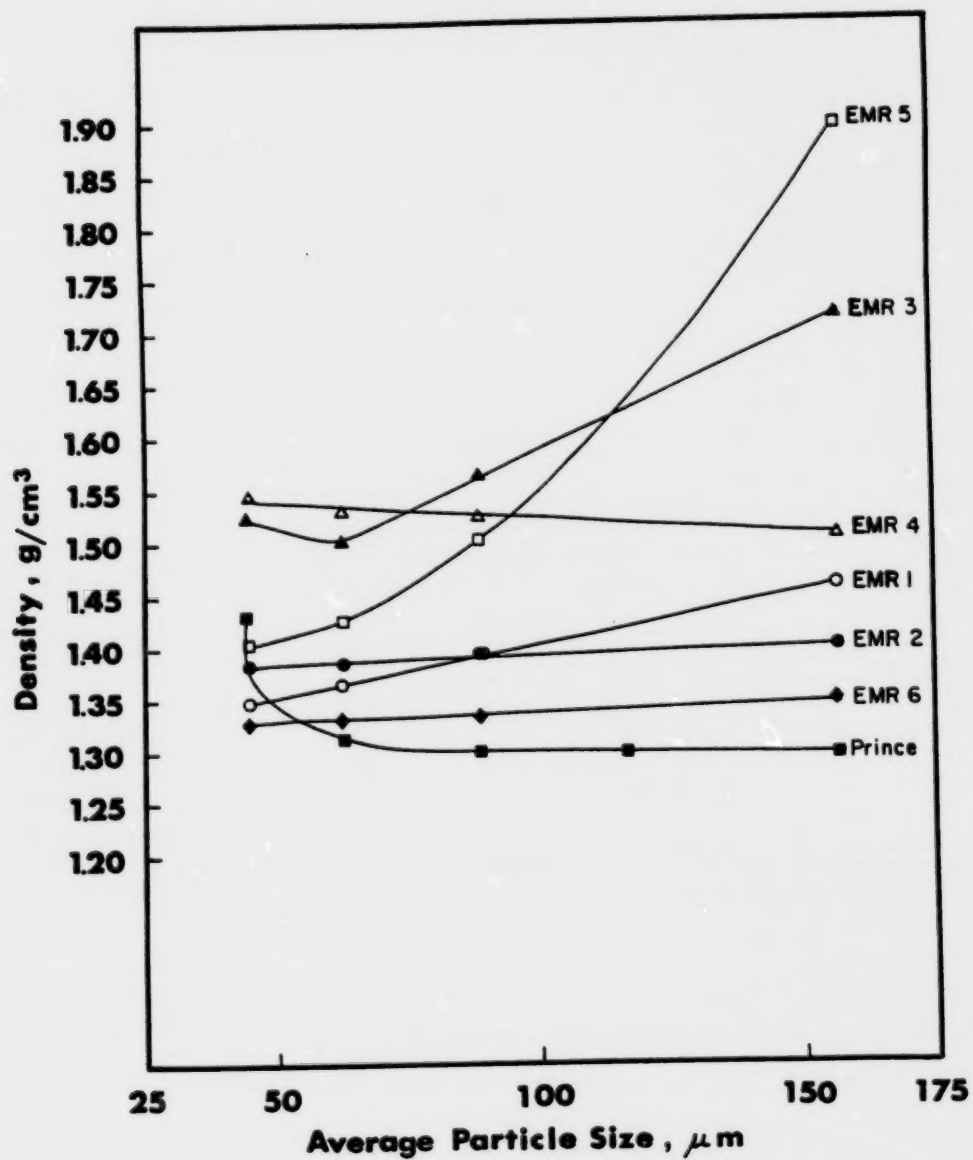


Figure 10: Effect of Particle Size on the Density of Western Coal Samples

variation in the pore structure but, as will be shown later, significantly impacted the surface characteristics of the coal.

Table 6 The Main Pore Structure Parameters For Prince Mine
Obtained From Mercury Intrusion Porosimetry

Time of Oxidation (hrs)	Surface Area (m ² g ⁻¹)	Vp (2-100 nm)
0	18	0.022
12	21	0.023
28	25	0.018
49	24	0.018
70	26	0.018
84	25	0.019
120	25	0.019

The water used in all tests was prepared by passing tap water through a Millipore RO unit, resulting in water of class II (1.6 mega ohms). The reagents used were analytic grade.

III RESULTS AND DISCUSSIONS

Study of coal wettability is complicated by the heterogeneous nature of its surfaces. It consists basically of a relatively hydrophobic organic matrix through which various hydrophilic sites (e.g. clay and shale minerals, moisture, highly-polar oxygen-containing functional groups) are interdispersed. The overall hydrophobic/hydrophilic balance depends on the coal's chemical and petrographic composition and generally increases the more extensive coalification process is. On the other hand, progressive weathering of coal surfaces results in decreasing its overall hydrophobicity through the formation of acidic functional groups (such as COOH, CO and phenolic OH) on previously hydrophobic sites. Such changes can take place with hardly any detectable variation in coal composition; however, its impact on beneficiation processes can be quite extreme.

III.1 Wetting Time

Over eight hundred and fifty experiments were conducted using this technique. The effect of coal's particle size, sample weight and the area of the surface on which it is deposited was investigated in order to determine optimum testing conditions with regard to reproducibility. Because of the multiplicity of critical contact angles obtained with different homologous series of organic compounds, it was decided to proceed with alcohol/water mixtures. In addition to the advantages of being readily available in all labs, such a system can give a wide range of surface tensions. Furthermore, this system is very close to the technically important MIBC/water frothing system.

To allow for comparison between samples of different weight, the data obtained were normalized in order to yield the time required for the wetting of 1 gm sample. No further treatment of the data was undertaken because of the lack of properly accepted theoretical background for this test.

III.1.1 Preliminary Investigations Using Eastern Coals

The dependence of wetting time on the particle size of Eastern coal is presented in Figure 2 from which it is evident that this parameter decreases sharply for particle sizes larger than 60 μ m. The reproducibility of these measurements was also found to be dependent on the particle size; thus for example the standard deviation (as measured from 6 replicas) was found to decrease from 25.3% down to 5.2% as the particle size increased from 60 to 90 μ m.

Normalized wetting times were also found to be strongly dependent on the weight of the sample tested (Figures 11 to 14) with larger samples tending to exhibit smaller wetting times. The reproducibility of the measurement was also found to be affected by the sample's weight, being largest for small samples. However, maximum reduction in scatter was found to take place when samples weight of 100 mg were used, and it was therefore decided to conduct the tests using 100 mg of -200 + 270 mesh samples in order to achieve best reproducibility while still retaining maximum sensitivity.

Wetting times were also found to be affected by the area of the liquid

surface on which they are deposited. This relationship is strongly dependent on the particle size of the sample tested. Thus, the wetting time of 60 μ m samples is reduced from 110 to 80 s/gm when the surface area is increased from 7.6 to 33.1 cm², whereas the corresponding values for 90 μ m samples are hardly affected (Figure 15).

A homologous series of straight-chain aliphatic alcohols (C₁-C₉) were used to determine the critical surface tension of the coal (Figure 16). A minimum was observed for propanol and a critical surface tension value of $\gamma_c = 26$ mN/m was obtained for this series. This value however differed greatly from similar observations obtained using benzene and its derivatives ($\gamma_c = 30$ mN/m, Figure 17) as well as those for alcohol/water system ($\gamma_c = 42$ mN/m). This multiplicity in γ_c (dependent on the type of homologous series utilized) was not reported in the literature and could most probably arise from specific interaction between the hydrophobic and hydrophilic sites on the coal's surface and the particular organic liquid used (e.g. aromatics, alcohols, etc.).

Having achieved acceptable reproducibility emphasis was shifted towards determining the relationship between wetting time and the degree of surface oxidation of coal. A series of coal methanol mixtures within the range of 15-40% by volume were tested for that purpose. This concentration range was selected because of the capability of linearizing the concentration-surface tension relationship within its bounds (Figure 18).

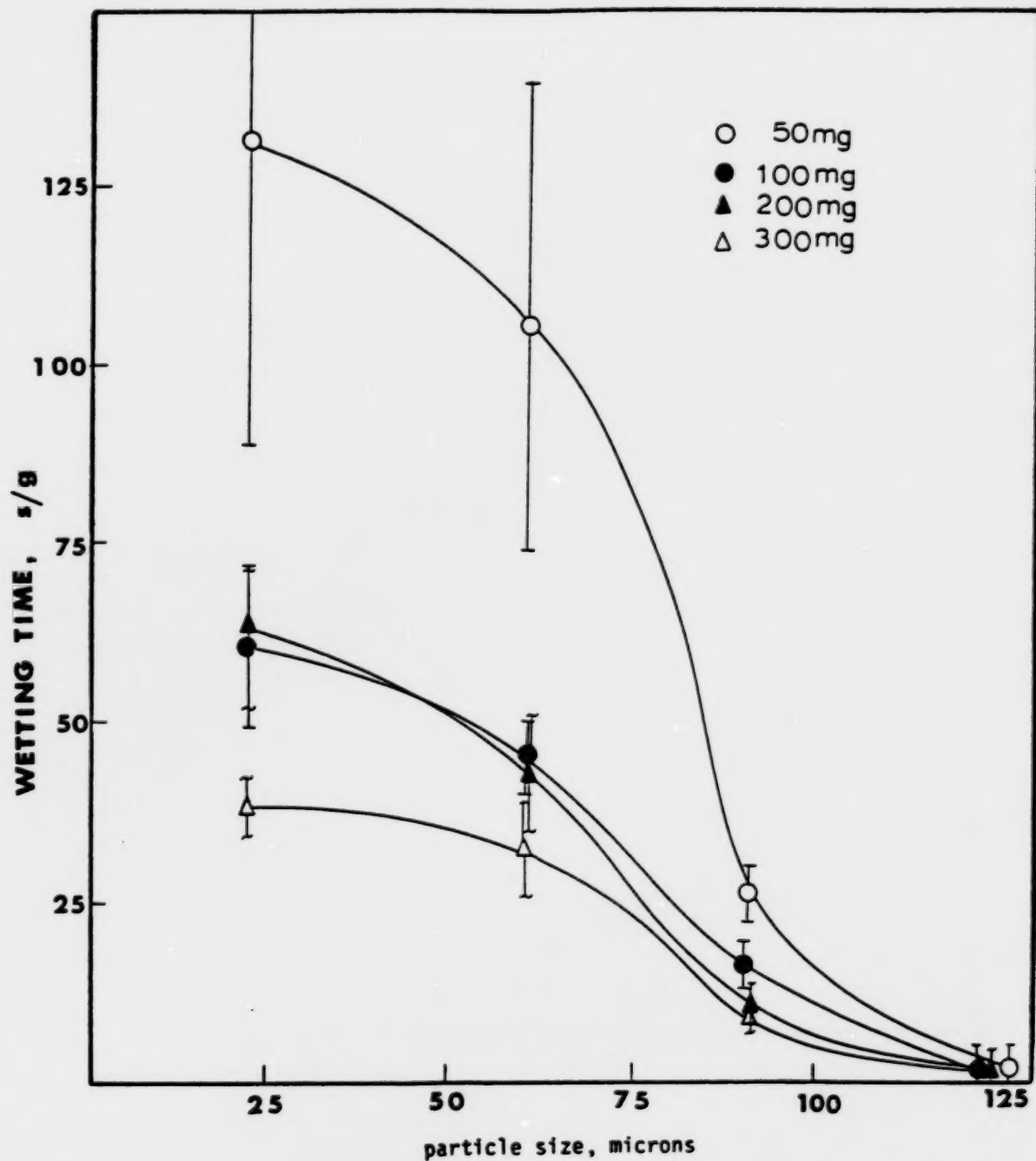


Figure 11 Effect Of Particle Size On the Wetting Time of Coal
(Coal Samples Wetted By 1-Butanol)

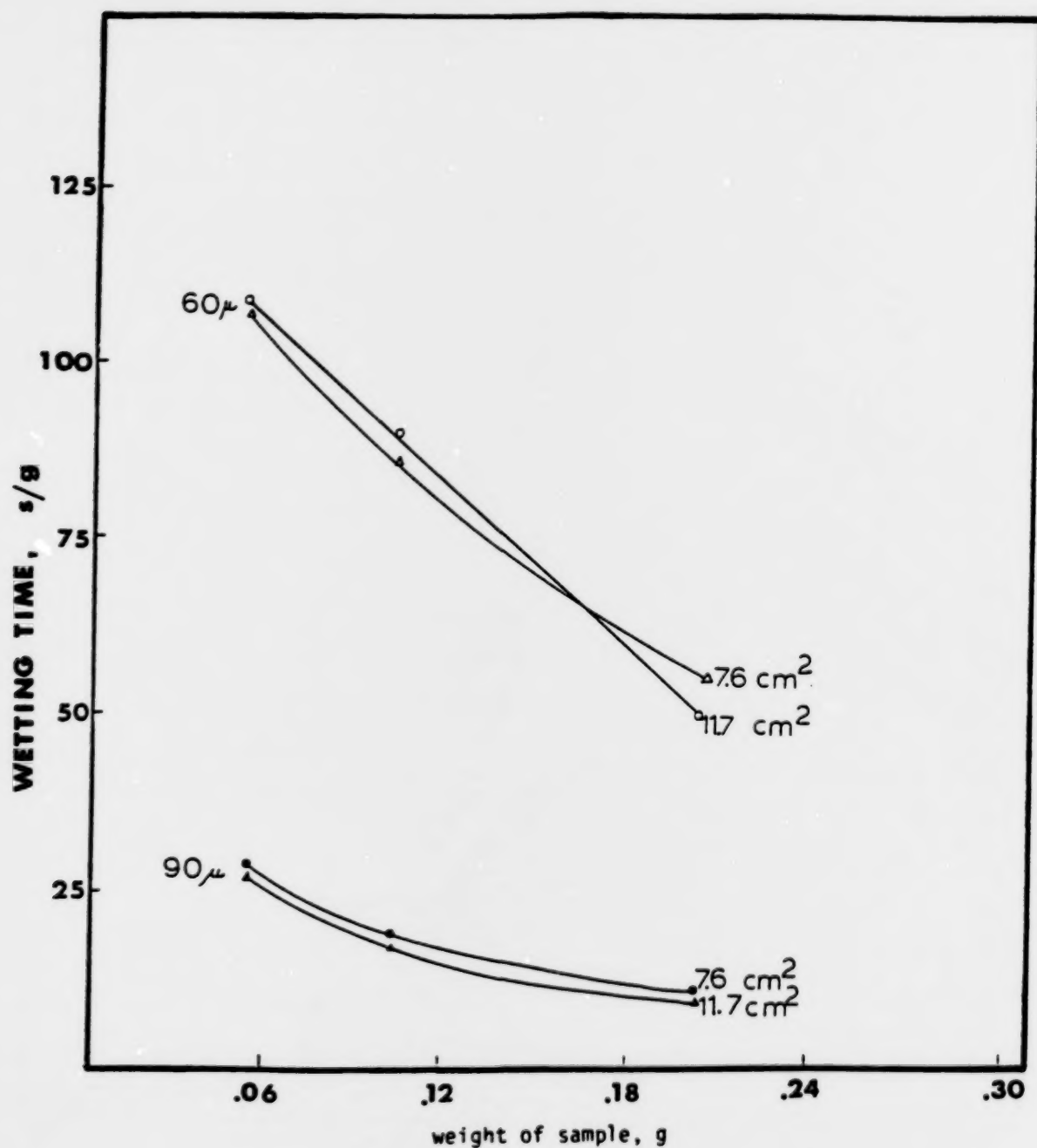


Figure 12 Effect of Sample Weight, and the Surface Area of the Liquid On Which It is Deposited, On the Wetting Time (No. 26 Metallurgical Coal Wetted by 1-Butanol)

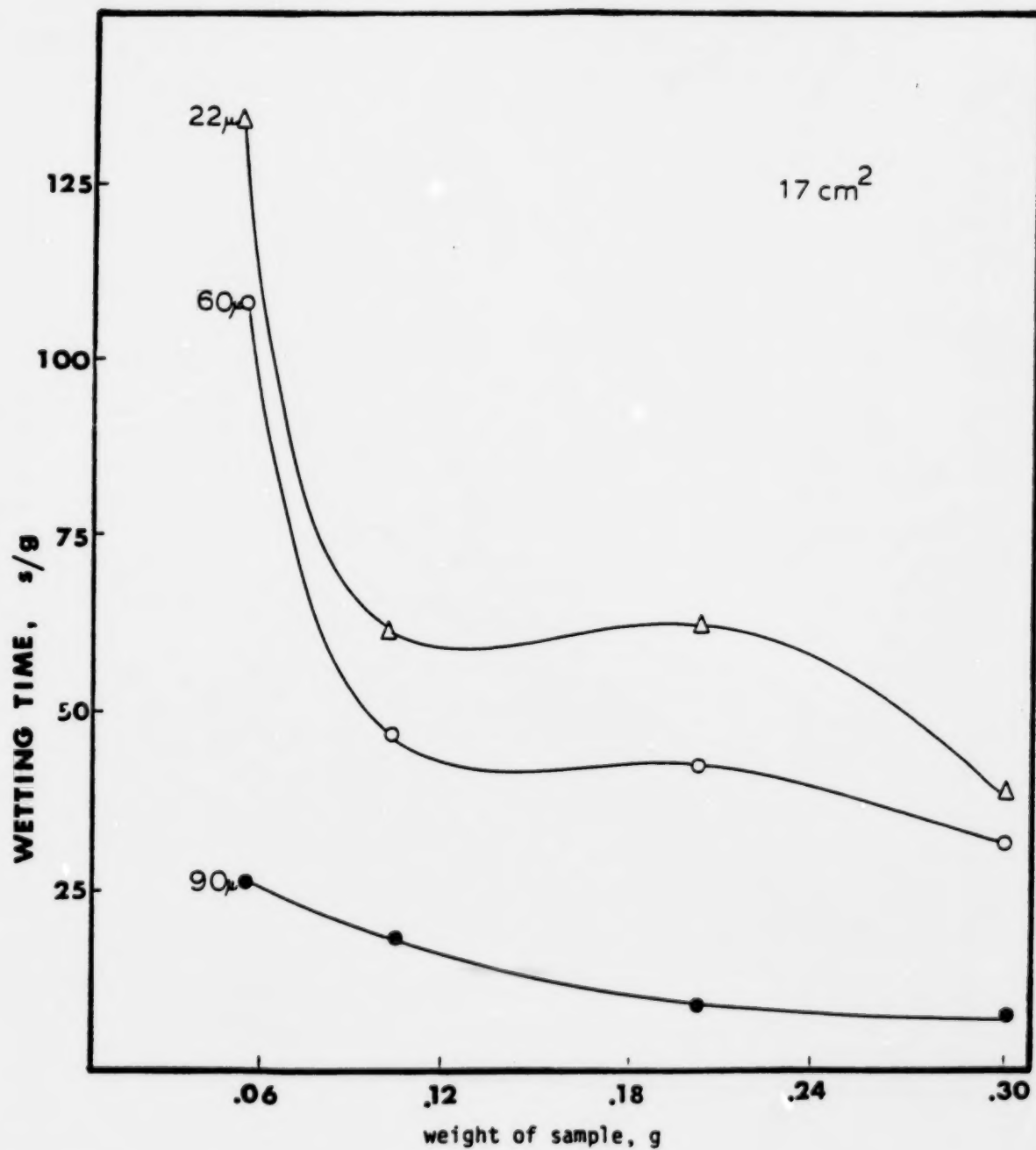


Figure 13 Effect of Sample Weight, and the Surface Area of the Liquid On Which It is Deposited, On the Wetting Time (No. 26 Metallurgical Coal Wetted By 1-Butanol)

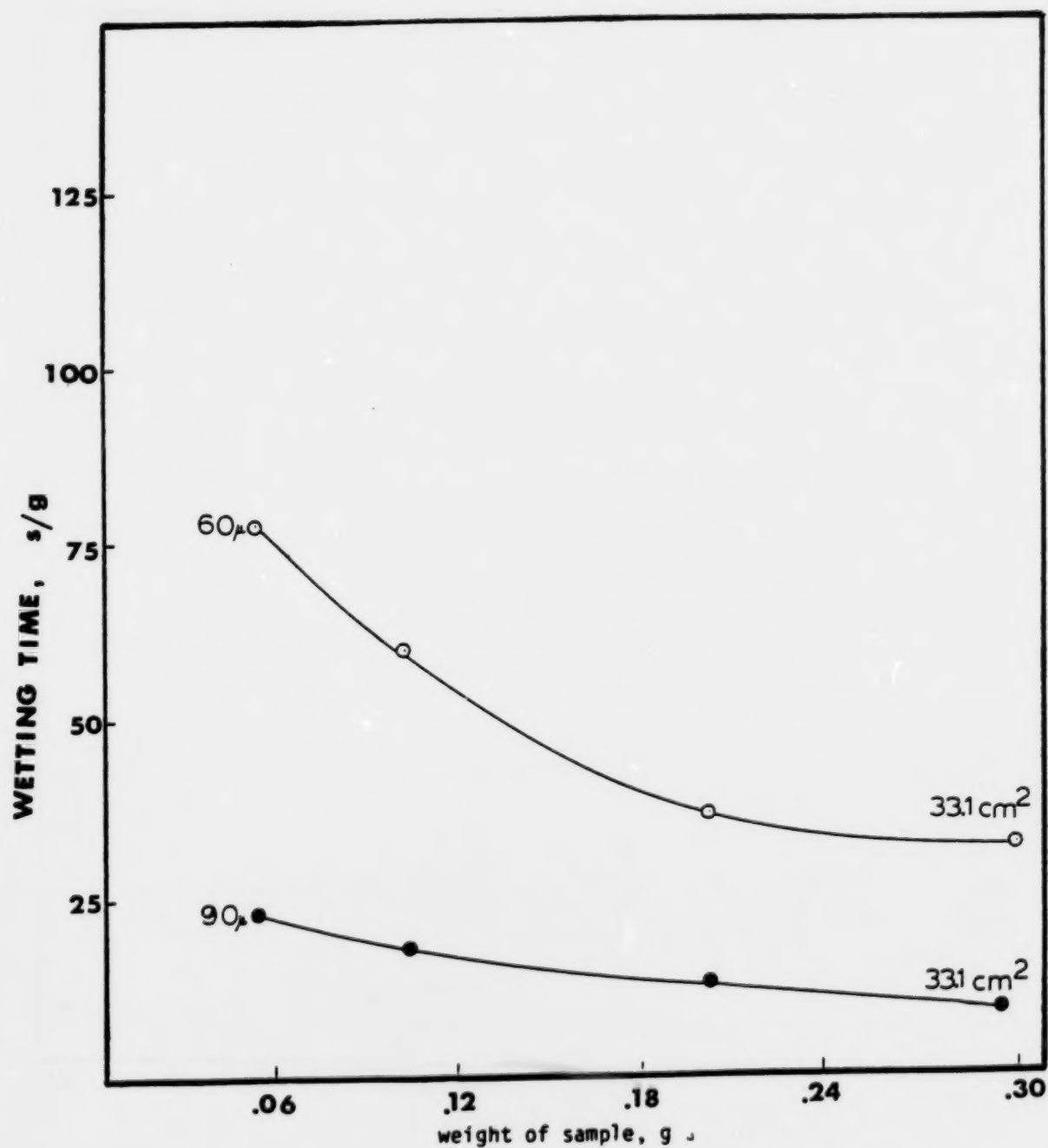


Figure 14 Effect of Sample Weight, and the Surface Area of the Liquid On Which It Is Deposited, On the Wetting time (No. 26 Metallurgical Coal Wetted By 1-Butanol)

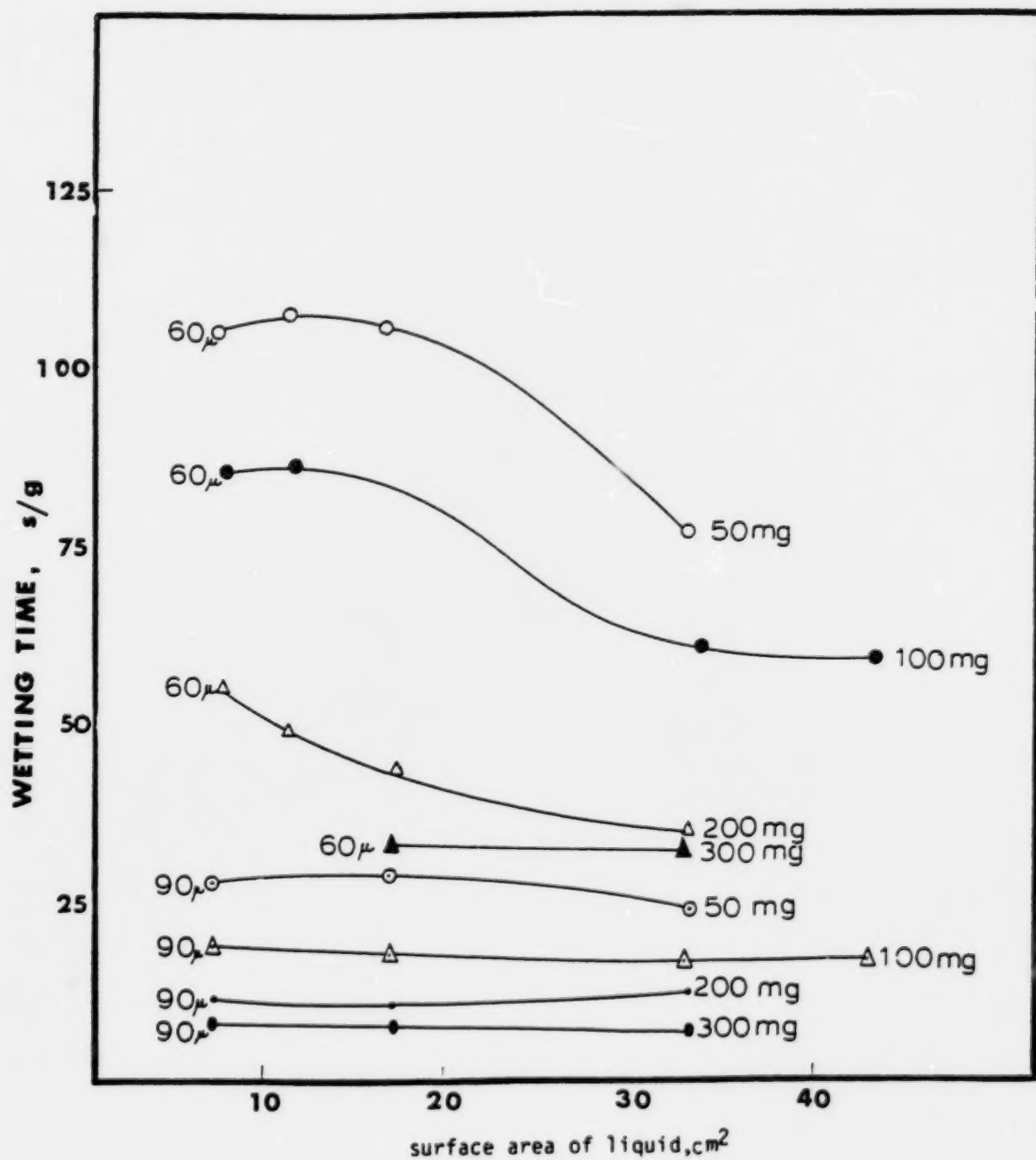


Figure 15 Effect of the Area of the Liquid On Which Sample Is Deposited In Its Wetting Time (No. 26 Devco Metallurgical Coal Wetted By 1-Butanol)

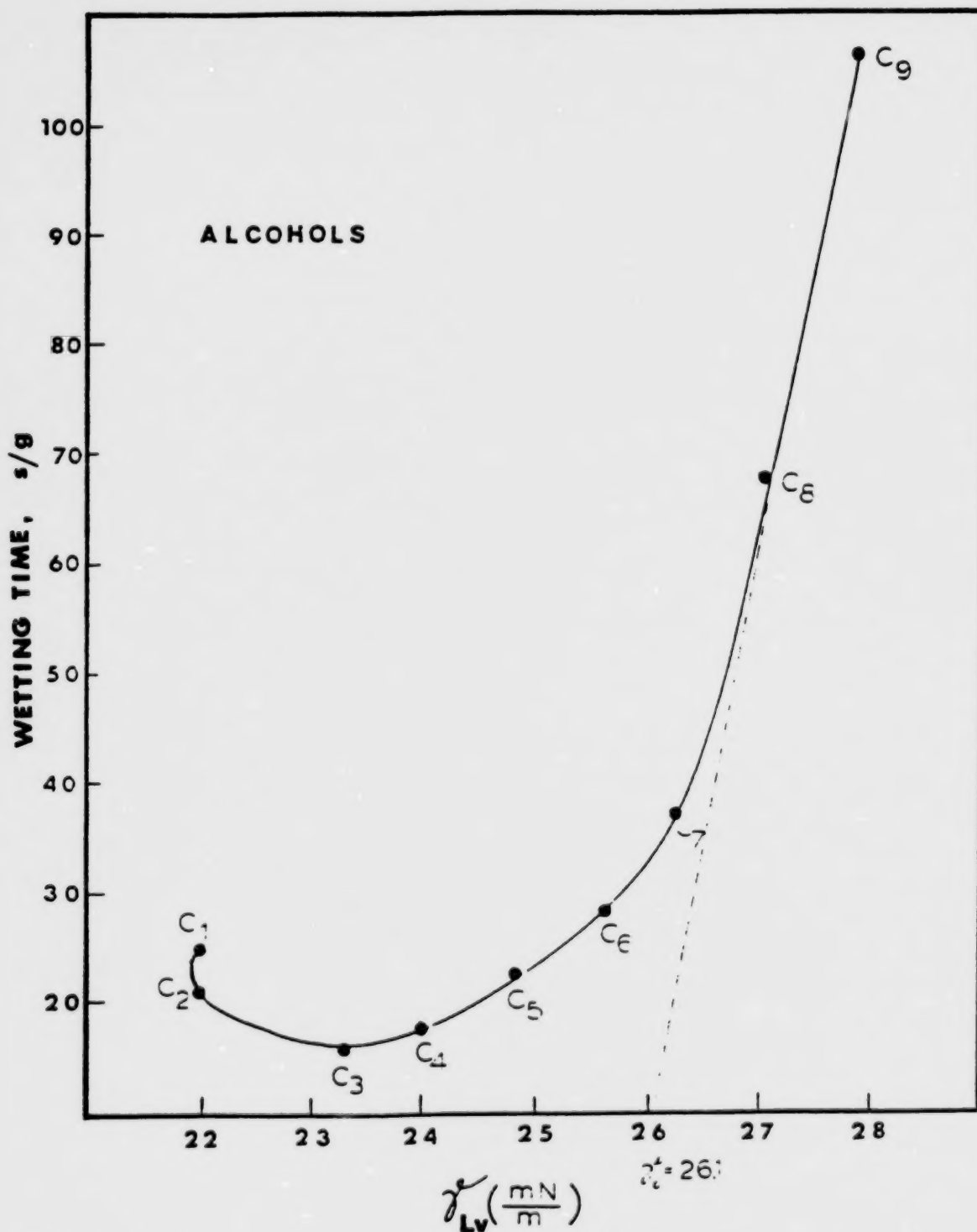


Figure 16 Effect of Surface Tension On Wetting Time (Prince Mine Coal Wetted By A Homologous Series of Aliphatic Alcohols C₁-C₉)

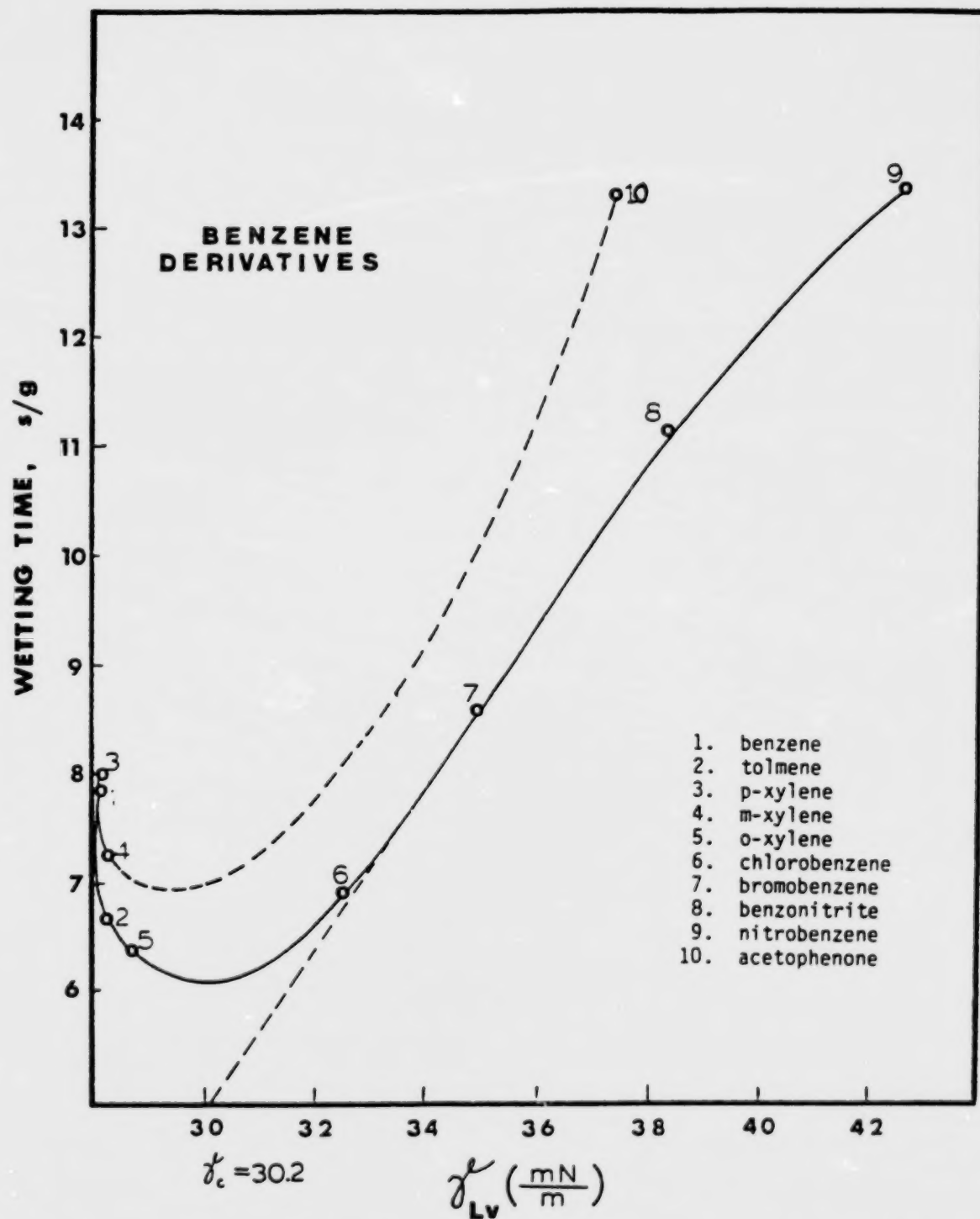


Figure 17 Effect of Surface Tension On Wetting Time (Prince Mine Coal Wetted By a Homologous Series of Aromatic Compounds)

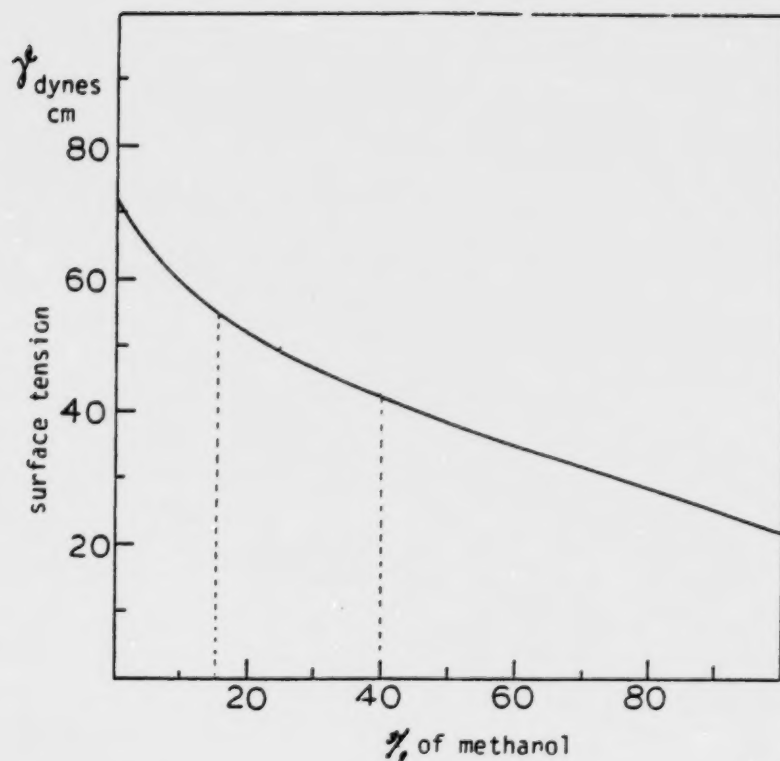


Figure 18 Effect of Methanol Concentration On Surface Tension of Methanol-Water Mixture

The impact of particle size on the wetting time in alcohol/water mixtures of various concentration is depicted in Figure 19, from which it became evident that particles larger than $120\ \mu\text{m}$ are affected very little by the methanol concentration. On the other hand, smaller particles ($80\ \mu\text{m}$) exhibit strong sensitivity to this parameter. This is systematically depicted in Figure 20 where wetting times exhibit a maximum at 25%. The same phenomenon was observed with other particle sizes but the peak at 25% is more pronounced (Figure 21).

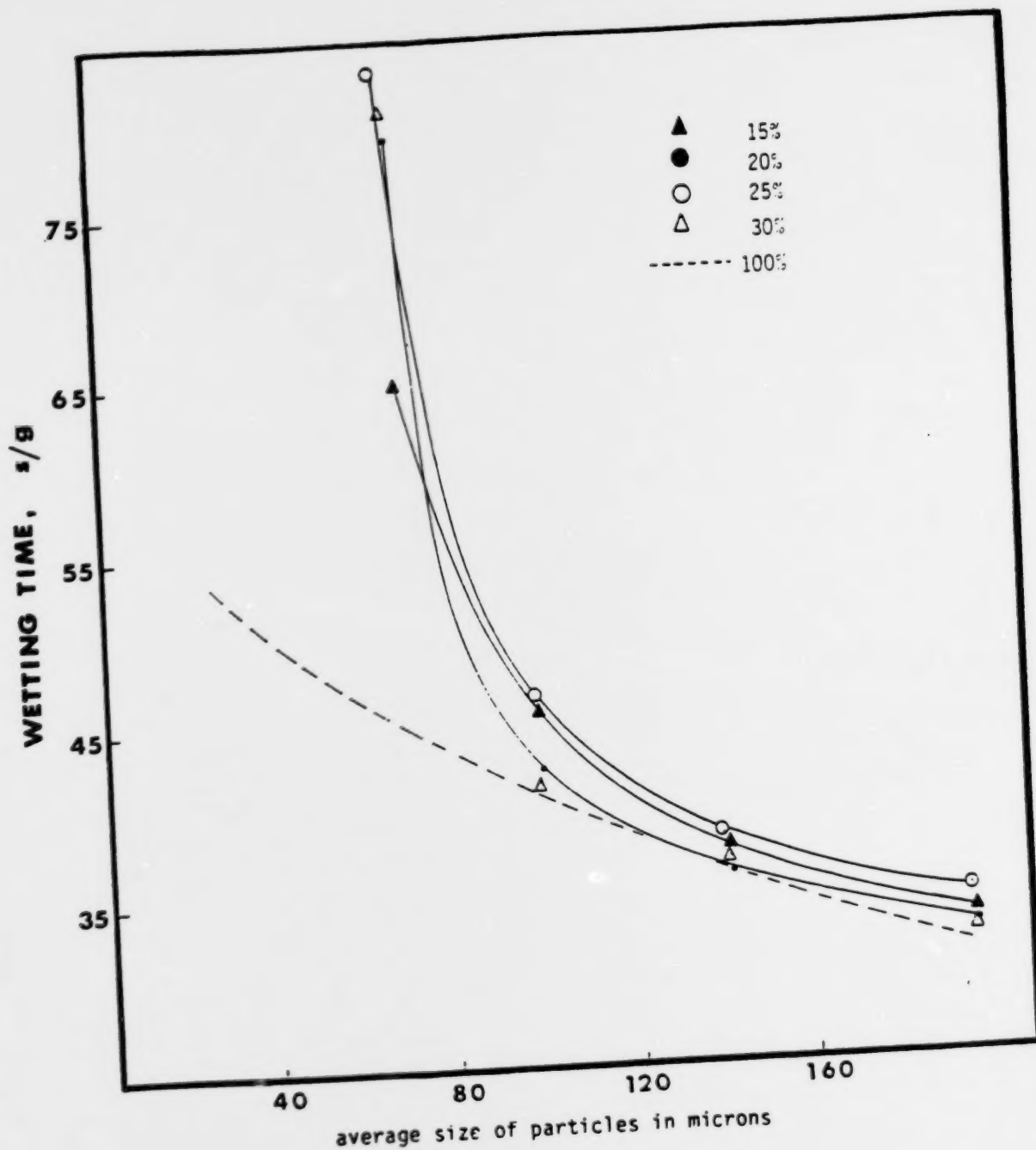


Figure 19 Effect of Particle Size On the Wetting Time of Coal (100 mg Samples of -200 +270 Mesh, Prince Mine Coal Wetted With Aqueous Methanol Solutions of Various Volumetric Concentrations)

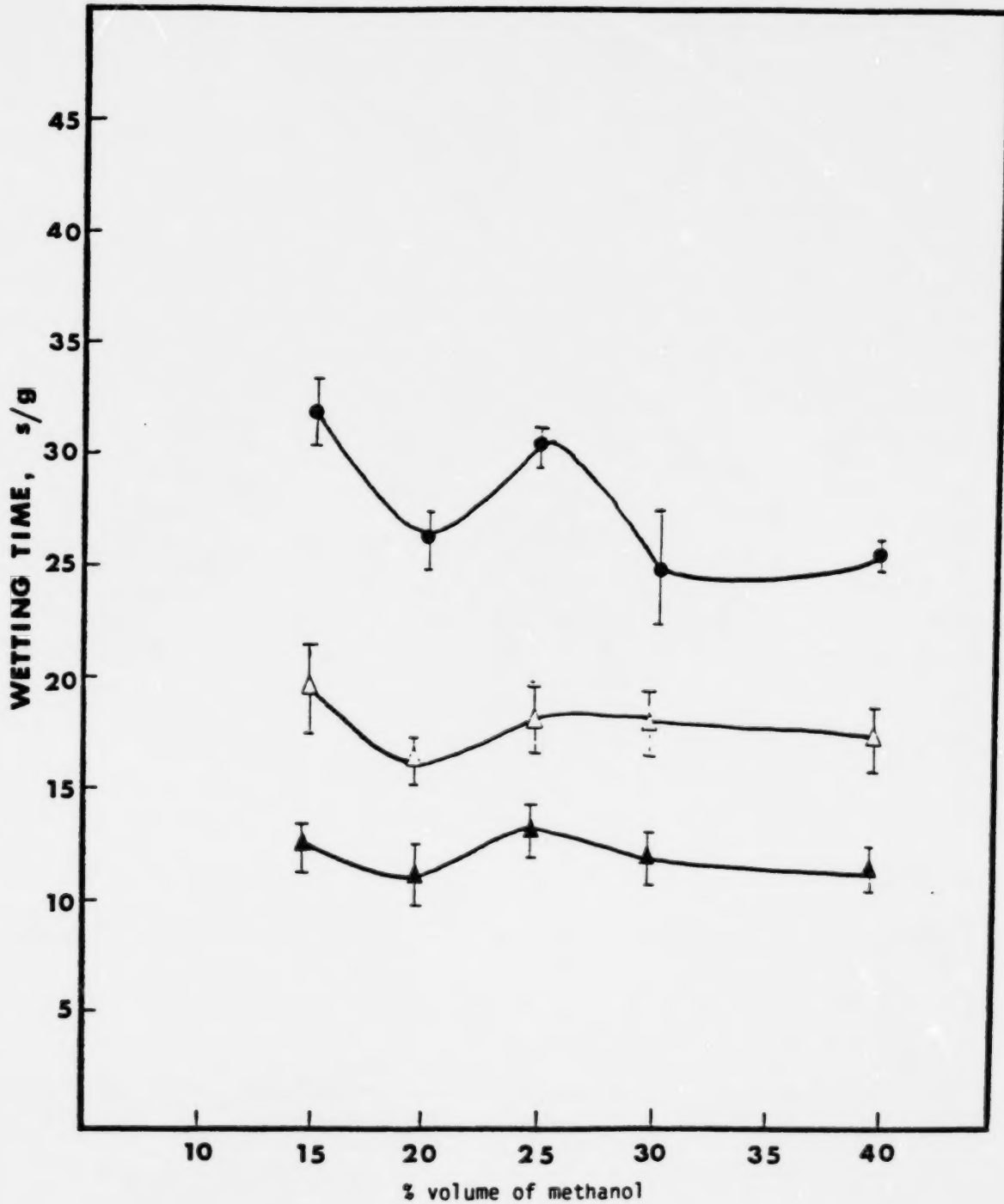


Figure 20 Effect of Methanol Concentration of the Wetting Time of Coal (100 mg Samples of Prince Mine Coal)

- (● -140 +200 mesh size)
- (△ -100 +140 mesh size)
- (▲ -70 +100 mesh size)

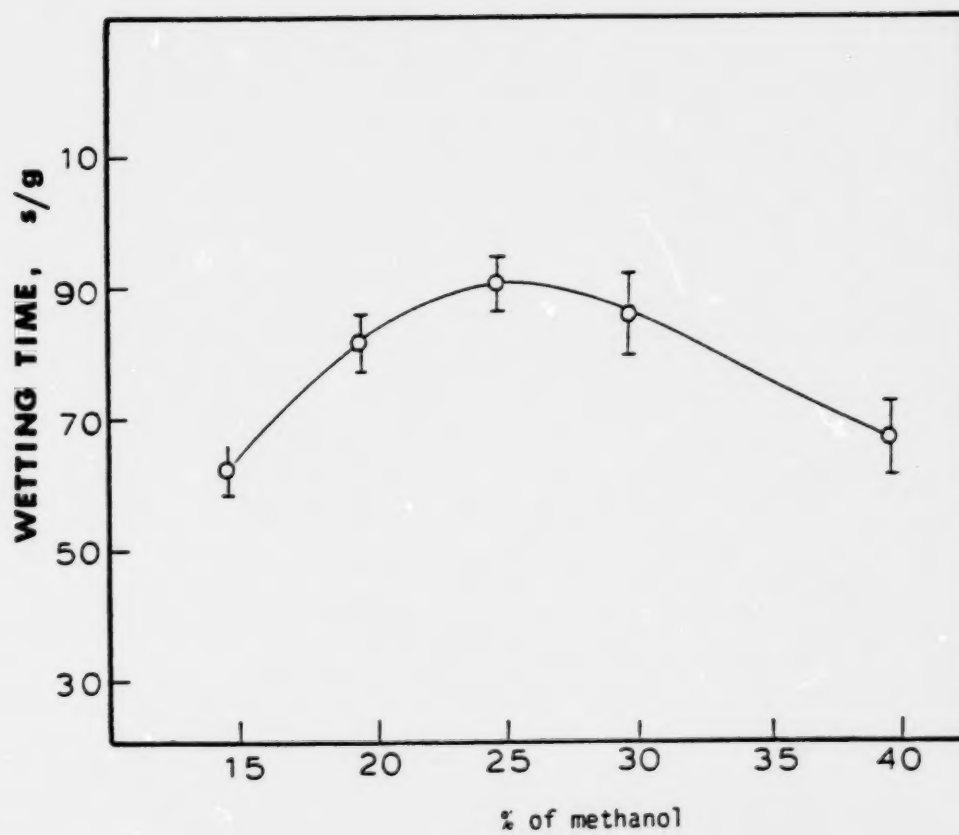


Figure 21 Effect of Methanol Concentration of the Wetting Time of Coal (100 mg Samples of Prince Mine Coal)
(-O- -200 +270 mesh size)

Preliminary testing indicated that the sensitivity of wetting-time-measurements to the degree of surface oxidation also exhibits a maximum at 25% by volume. Further testing was, therefore, undertaken using 100 mgs of -200 + 270 mesh coal samples, using methanol/water mixture (25% by volume methanol) as a wetting liquid.

The capabilities of this relatively simple test to distinguish between the surface characteristics of progressively oxidized coals as well as coals stemming from various seams is clearly depicted in Table 7 and Figure 22.

Table 7 The Wetting Times For Coals of Different Place of Origin

Sample	Wetting Time* (sec/g)
Prince Mine	90
Princess	58
DEVCO No. 26	43
Evans	41
Lingan	38

*Wetting time measured for samples -200 +270 mesh size in 25% volume methanol

Part of this difference could possibly be attributed to variation in density but the distinction is too large to be completely attributed to this factor alone.

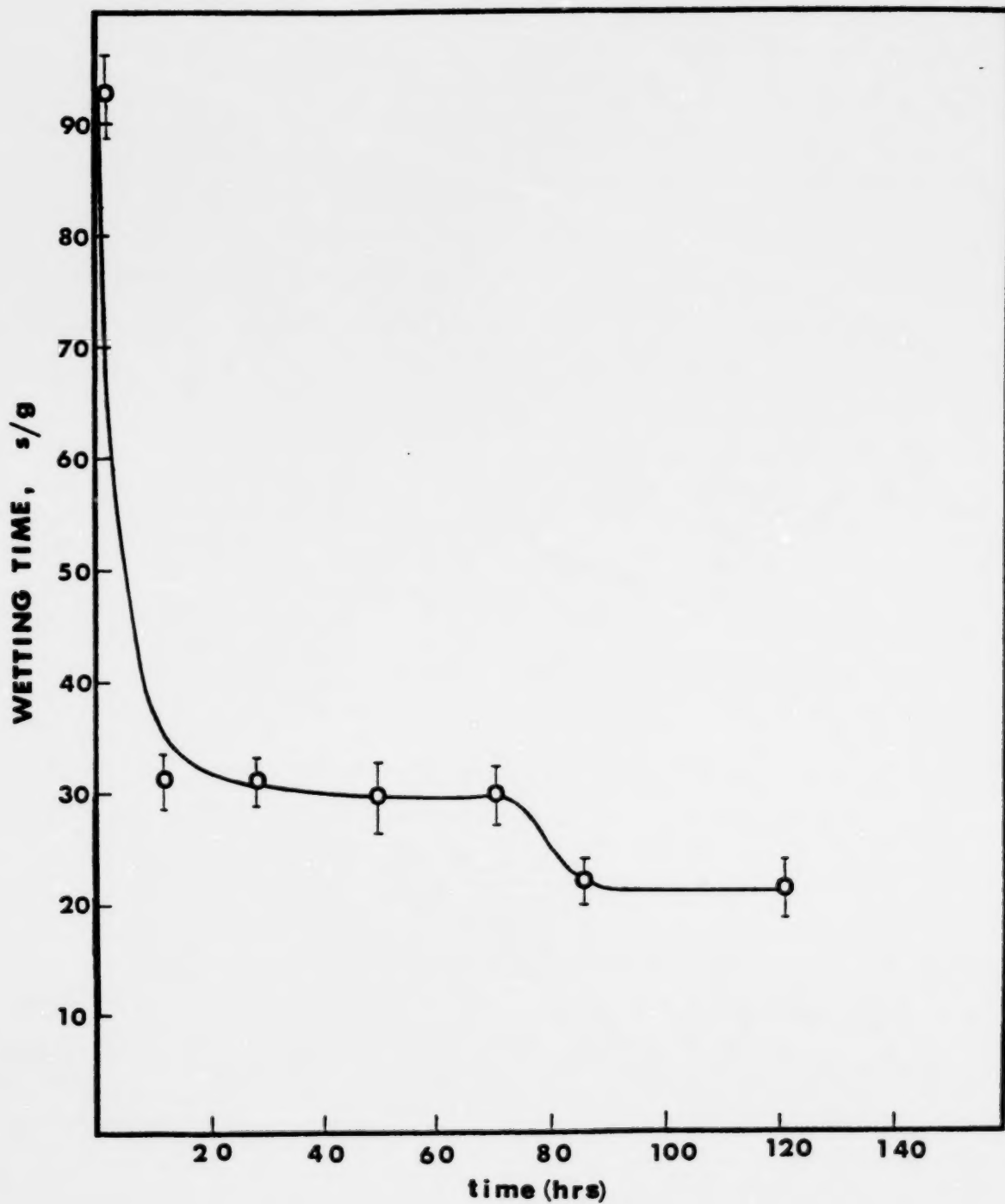


Figure 22 Effect of Surface Oxidation on the Wetting Time of Coal (100 mg Samples of -200 +200 Mesh Prince Mines Coal Wetted By 25% volume Aqueous Methanol Solution)

All wettability measurements are strongly affected by the interaction between the wetting liquid and the surface of the coal. The results obtained are, therefore, expectedly strongly dependent on the extent and orientation by which the liquid component is adsorbed on the surface of the coal. This phenomenon can be made use of to increase the sensitivity of the "wetting time, or Walker" test to coals of different degrees of hydrophobicity. This could be accomplished by varying the hydrophobic/hydrophilic balance in the testing liquid through variation of its alcohol content.

The strong dependence on the nature of the liquid is clearly demonstrated by the data obtained using n-hexanol (Figure 23). In a manner analogous to water/alcohol solutions, slight oxidation of the surface was found to decrease the time needed for wetting the coal. The sensitivity is much less than that of the water/alcohol system but the most remarkable difference was observed at highly oxidized coals where the wetting times were found to jump after 124 hours. This is most probably due to a reversal in the orientation by which hexanol molecules adsorb on the surface at high levels of surface oxidation.

III.1.2 Reproducibility of Immersion Time Technique

Table 8 presents the variation in the reproducibility of this technique as a function of both particle size and type of liquid used. Highest reproducibility was obtained using -200 + 270 CSA mesh coal samples wetted by 25% aqueous methanol solutions.

The next most important factor in determining the reproducibility of this test is the weight of the sample (Table 9) followed by the area of the surface on which they are deposited (Table 10).

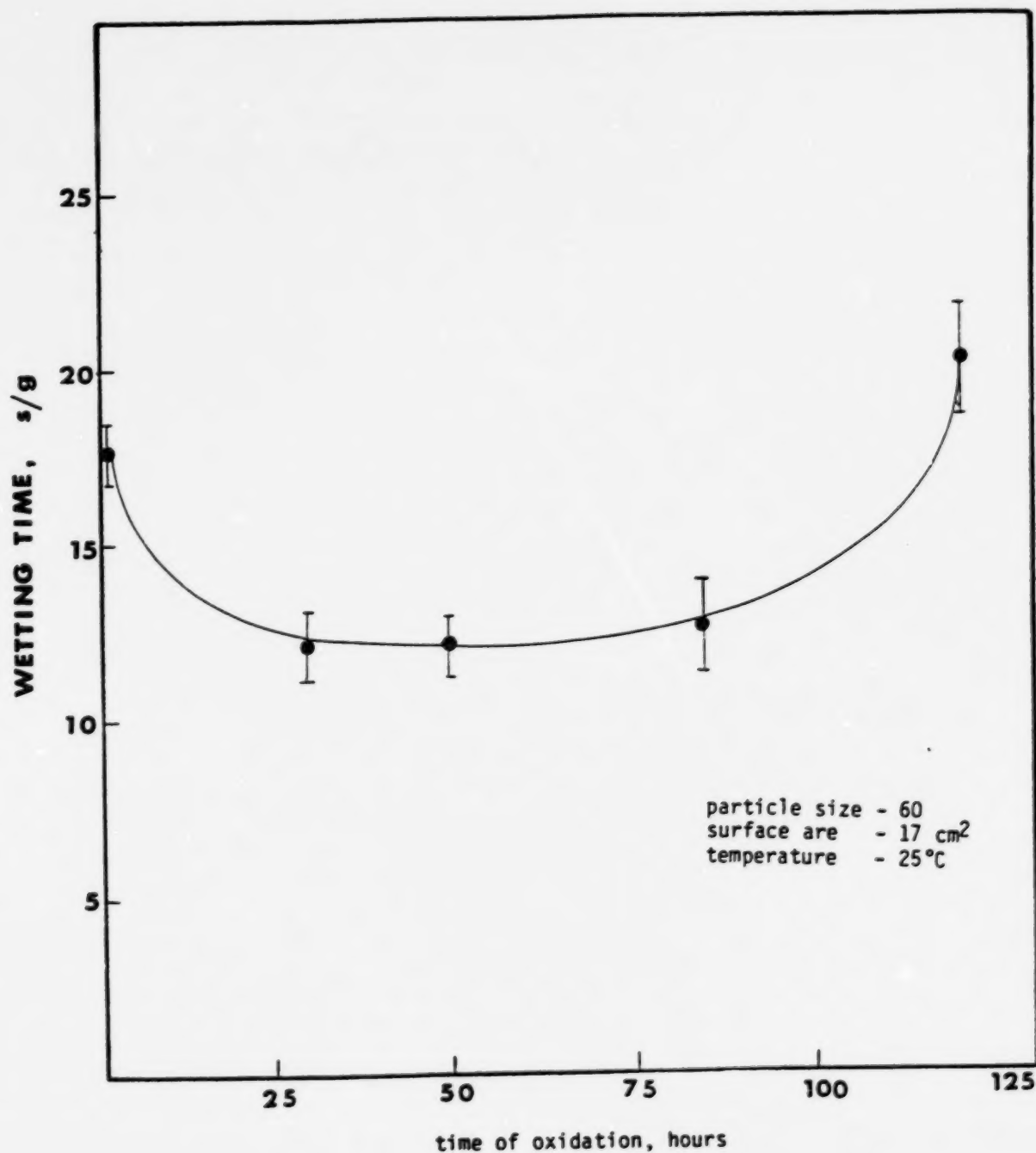


Figure 23 Effect of Coal Oxidation on Wetting Time (100 mg Sample of Prince Mine Coal -200 +270 Wetted by n-Hexanol)

TABLE 8 Reproducibility of Immersion-Time Technique (Prince Mine Coal)

Particle Size	N**	σ n-1/X (% age)				
		*15% methanol	20%	25%	30% methanol	100%
-270	5	14.7	38.2	14.4	6.9	
-200 +270	6	7.2	4.5	5.4	6.8	
-140 +200	7	5.1	5.6	3.7	10.5	sank immediately
-100 +140	6	11.9	7.1	8.7	8.9	
-70 +100	6	5.2	11.5	6.6	5.6	

* Aqueous methanol/volumetric concentration

** Number of replicates

TABLE 9 Effect of Sample Weight on Immersion-Time Reproducibility*

Particle Size (m)	No. Replicates	σ n-1/X (% age)			
		50 mg	100 mg	200 mg	300 mg
		Surface 33 cm ²			
60	5	19.3	7.4	15.5	17.8
90	5	13.4	6.3	4.2	8.2
128	5	Sank immediately			
		Surface 17 cm ²			
22	9	32.6	19.9	15.3	9.2
60	7	30.2	9.3	25.3	24.0
90	5	8.0	8.2	5.2	8.8
128	2	Sank immediately			

*Wetting liquid - n-butanol at 25°C

TABLE 10 Effect of Surface Area on Immersion-Time Reproducibility

Particle Size (μ m)	No. Replicates	σ_{n-1}/X (% age)				
		7.6	11.7	17	33	43
22	5	-	-	9.2	9.0	-
60	5	8.4	25.7	23.8	7.4	20.1
90	5	6.0	21.6	8.8	6.3	14.6

*Surface area of liquid on which sample is deposited, cm^2

Coal oxidation was found to adversely affect the reproducibility of this test regardless whether this oxidation was induced at an accelerated rate in the lab (Table 11) or whether it is due to other natural reasons (Table 12).

TABLE 11 Effect of Coal Oxidation on Reproducibility of Wetting Time
Technique (Prince Mine Coal)

Oxidation Time (hr)	No. Replicates	σ_{n-1}/X (% age)	
		25%*	20%
0	6	5.4	4.5
14	6	7.1	7.8
28	6	6.4	9.1
49	5	11.8	9.0
72	5	8.5	4.9
84	7	8.2	4.9
120	6	13.2	7.2

*Concentration % volume of aqueous Methanol solution

TABLE 12 Effect of Coal Origin on the Reproducibility of Wetting Time

Origin	No. Replicates	Wetting time sec/g	$\sigma_{n-1/X}$ (% age)
Prince	6	89.1	5.4
Princess	7	58.8	5.3
Evans	7	44.0	4.3
DEVCO No. 26	7	43.9	2.9
Lingan	6	35.3	12.1

III.1.3 Application To Western Coal Samples

The surface characteristics of the Western coal samples were evaluated using 100 mg samples of the -200 +270 mesh fraction deposited on 25% aqueous methanol solution. These conditions were selected because they were found to result in highest reproducibility and sensitivity to oxidation, in the case of eastern coals and the results obtained are shown in Figure 24. To test the validity of this assumption reproducibility tests were conducted in quadruplicates and the data obtained are reported in Table 13.

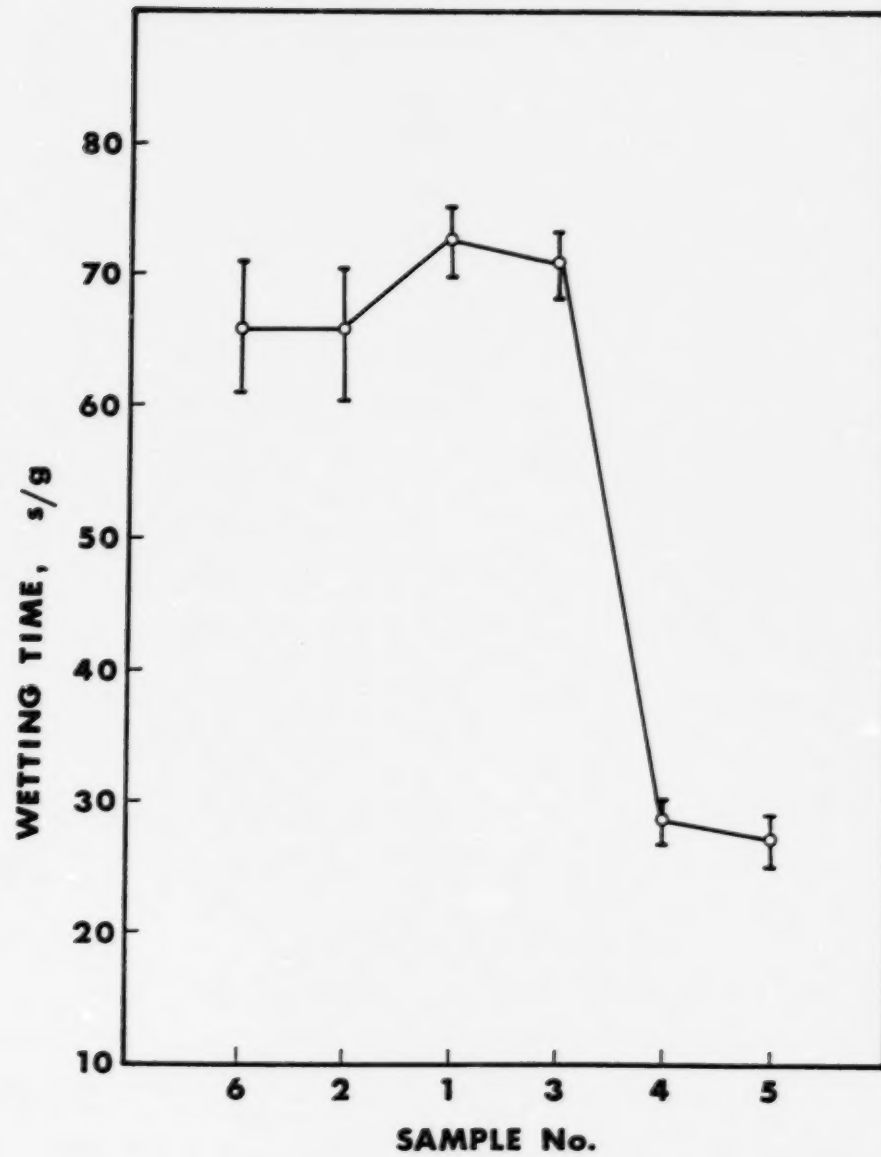


Figure 24 Immersion Times For Western Coal Samples

Table 13 Reproducibility of Immersion-Time Tests When Applied
To Western Coals

	Sample No.					
	1***	2**	3	4	5	6*
Immersion- Time (secs)	7.18	6.87	7.22	2.77	2.70	7.03
	7.41	5.43	7.20	2.91	2.80	6.53
	6.68	6.99	6.94	2.65	2.34	6.74
	7.33	6.12	6.64	2.90	2.77	5.85
Average	7.15	6.48	7.00	2.81	2.65	6.54
n-1	0.33	0.53	0.27	0.12	0.21	0.50
Error %	±4.6	±8.2	±3.9	±4.4	±8.0	±7.7

*small amount left on surface

**a lot left on surface

***heavy film over entire surface with a lot of coal on it

A very high degree of reproducibility (<5%) was observed in conjunction with samples 1, 3 and 4. The larger variance observed while testing coal No. 5 can be attributed to the shortened immersion time, while those observed in conjunction with samples No. 6 and 2 can be attributed to the presence of highly-hydrophobic powdered macerals in the sample.

III.2 The H-E Method

Reasonably good pellets were formed under the pressures investigated; however, liquids placed on their surfaces were imbibed by the pellets rather than forming distinguishable drops on the surface. This phenomenon persisted regardless whether the pellet was dry or pre-saturated with liquid and was found to occur with wetting (C Cl₄, Hexyl alcohol, formamide) as well as with none wetting liquids (water, ethylene glycol).

Coal powders (-100 + 200 mesh) were then used to prepare pellets under compaction pressures varying between 5,000 and 10,000 psi. Two different techniques for pre-saturating the pellets were tested. In the first liquid was continuously dropped on the pellet surface whereas in the second approach a liquid mist was utilized.

Drops could be formed with difficulty on the surface of pellets formed at pressures equal to or larger than 8,000 psi. The drops remained on the pellets' surface for only a few minutes during which they were continuously receding due to imbibition. The time a drop is retained on the surface of a pellet was found to increase when finer coal powders were used (-200 + 270 mesh) and as the compaction pressure was increased to 50,000 and 100,000 psi.

Thin layers of what appears to be clay minerals were observed on the surface of water and the measured contact angles of the receding drops were found to range between 4° and 15° . This contradicts strongly with the value of 92° measured on cleaned surfaces of the same coal. A small part of the difference would be attributed to the roughness of the cleaned coal surface and to the porosity of the pellet; however, the extremely small value measured suggest that the hydrophillic components of coal strongly interfere with the results of this technique.

It was observed, however, that the rate at which a drop is imbibed by a pellet is dependent on its porosity, the hydrophobicity of its surface. Thus for example, under otherwise constant experimental conditions the extent of

surface oxidation was found to strongly influence the time needed for complete imbibition of liquid drops (Figure 25).

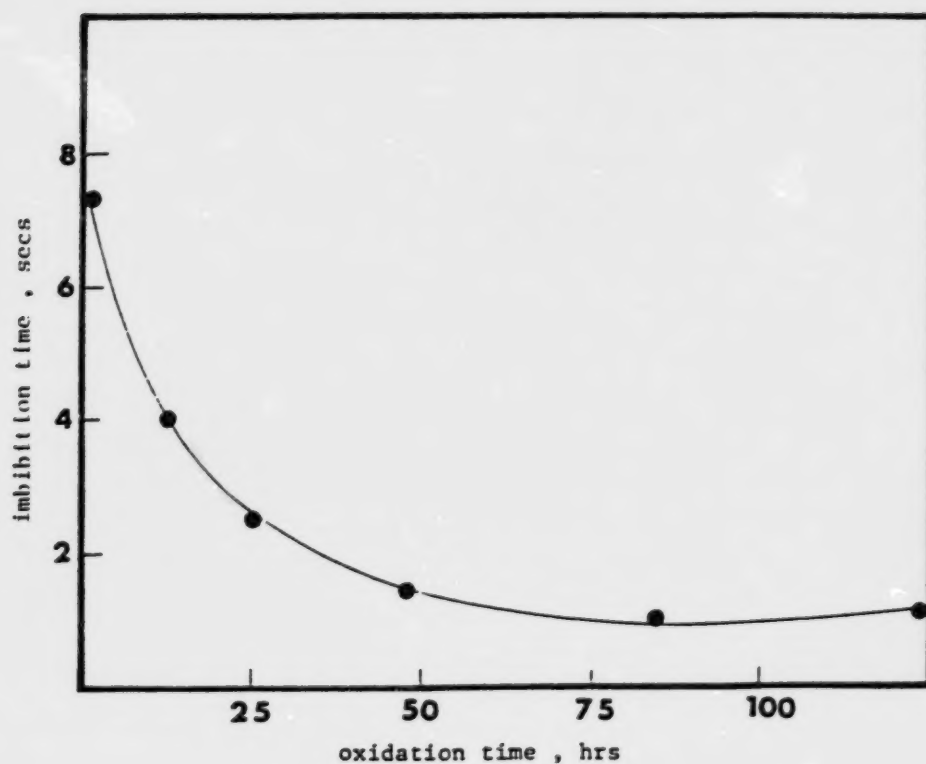


Figure 25 The Influence of Coal Oxidation on the Imbibition Time of Water Droplets. (-200 +270 Mesh Coal Pelletized Under 100,000 psi Pressure, Drop Volume = 0.015 ml)

A total number of 92 experiments were conducted using this technique.

As previously mentioned these measurements are very difficult to obtain, and the few ones evaluated are in discrepancy with what is known about the wettability of the coal matrix. The H-E. measurement is, therefore, much more indicative of the surface properties of the shale component of coal.

On the other hand, while conducting these tests it was found that the time required to drain a 0.015 ml drop placed on the surface of a pellet compacted at 100,000 psi were found to be highly reproducible and are strongly affected by the extent to which coal is oxidized (Table 14)

TABLE 14 Effect of Coal Oxidation on the Reproducibility of
Imbibition Time Measurements*

Oxidation Time (hr)	No. of Replicates	Time (X) (sec)	$\bar{x} - 1/X$
0	6	7.25	5.9
14	6	4.02	4.6
28	6	2.55	3.7
49	6	1.80	4.8
70	6	1.20	4.6
84	6	1.06	8.6
120	6	1.17	8.6

*0.015 ml drop placed on pellets compacted at 100,000 psi.

Because of the lack of success in applying the H-E method with the rather hydrophobic Eastern coal samples, it was decided not to test it with the more hydrophillic Western coals.

III.3 Capillary Pressure Due Liquid Imbibition in Powder Beds

This technique relies on measuring the air pressure required to prevent further penetration of the wetting liquid into a vertical bed of compacted solids. It is therefore not only dependent on the interfacial forces at the liquid/solid/air system but also on the capillary structure of the bed tested.

This factor has resulted in poor reproducibility ($\pm 30\%$ on the average) when the sample-preparation techniques mentioned in the literature were utilized. Successive trials to improve reproducibility ultimately led to the adoption of the ASTM standard D4164-82 (for compaction of catalyst) with the result that the average error was brought down to $\pm 10\%$.

III.3.1 Preliminary Investigations Using Eastern Coals

The results obtained using Prince Mine coal of different degrees of oxidation are depicted in Figure 26 from which the ultimate capillary pressure can be derived by extrapolation to values of zero (Figure 27). The data clearly show that the capillary pressure increases with increasing levels of oxidation with the sensitivity being highest at low levels of oxidation.

This technique suffers, however, from the length of time needed to approach equilibrium, a situation which can take up to four hours. A total of 42 experiments were conducted using this technique.

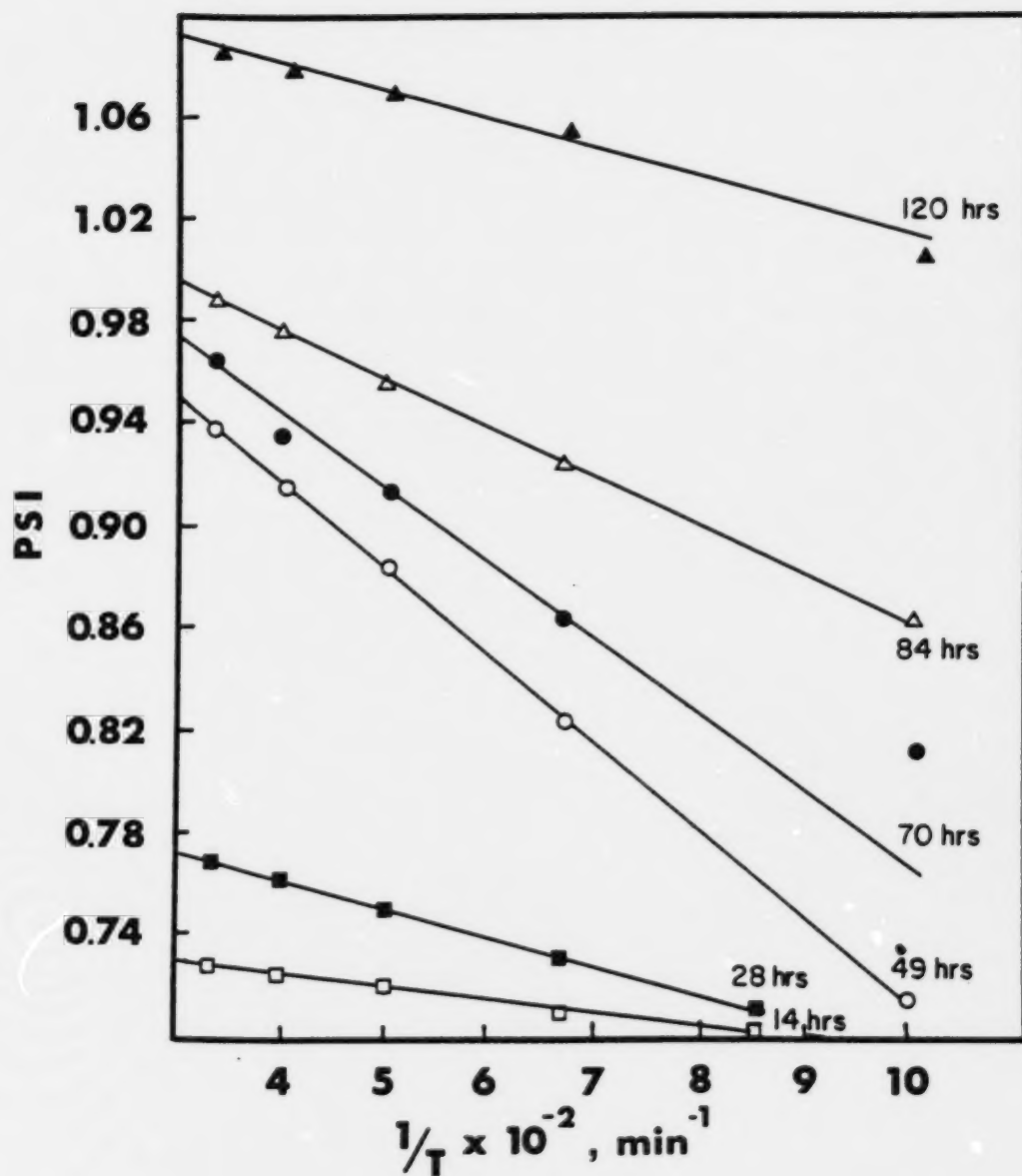


Figure 26 Variation of Capillary Pressure For Prince Mine Coal Oxidized To Various Extents and Wetted By 25% Volume Methanol (2 gm Samples -200 +270 mesh, tapped 150 times)

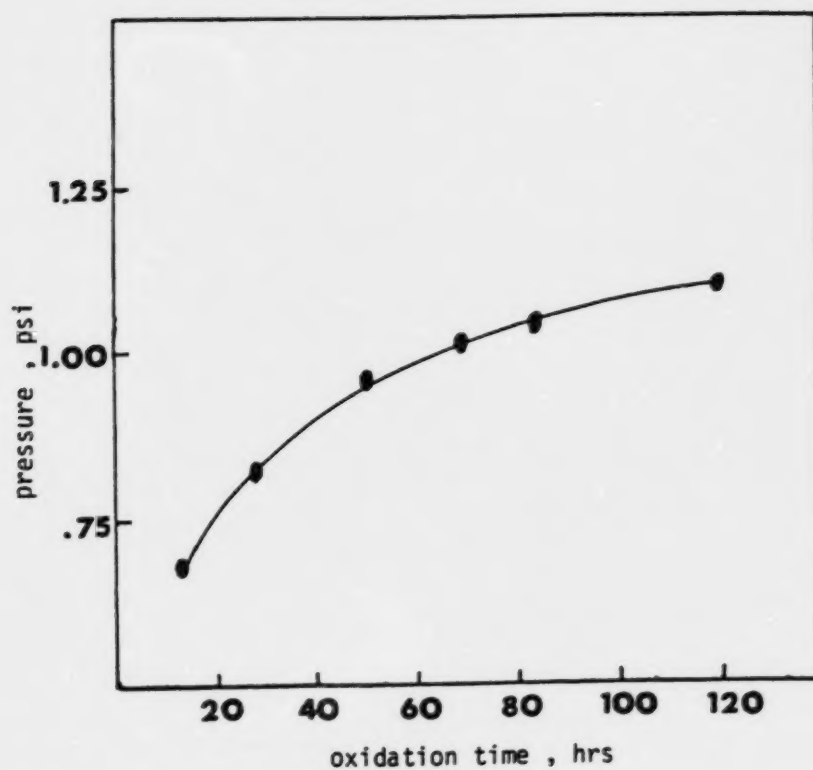


Figure 27 Variation of the Capillary Pressure For Oxidized Sample of Prince Mine Coal (-200 +270 mesh size, wetting liquid 25% methanol)

III.3.2 Evaluation of Reproducibility

Progressive oxidation of coal was found to beneficially affect the reproducibility of this technique (Table 11), thus progressively reducing the error from $\pm 15\%$ down to 2% for coal oxidized up to 120 hours. This phenomenon arises from the progressive reduction in the relative magnitude of the random error with decreasing coal hydrophobicity. On the other hand a systematic error is introduced since variations in liquid levels within the bed are not accounted for. This deviation could be as high as 8% in some cases.

TABLE 15 Effect of Coal Oxidation on the Reproducibility
of Capillary Pressure Technique*

Oxidation Time of Sample	No. Replicates	Mean Value (psi)	Standard Deviation	$\sigma_{n-1/X}$ (% age)
0	6	1.04	± 0.10	9.6
14	6	0.74	± 0.11	14.9
28	6	0.78	± 0.09	11.5
49	6	0.97	± 0.06	6.2
70	6	1.00	± 0.04	4.0
84	6	1.01	± 0.02	2.0
120	6	1.10	± 0.02	1.8

*-200 +270 coal samples wetted by 25% volume aqueous methanol solution.

III.4 Dynamic Penetration of Liquid Through a Powder Bed

In this technique the rate of weight gain through liquid imbibition in a compacted bed of coal is monitored. As is the case with the capillary pressure method, this technique is very sensitive to the technique by which the coal sample is compacted. Adoption of the ASTM standard compaction method

reduced the average error from 2% down to 5%. The permeable surface on which the coal bed is supported also had to be modified in order to improve the responsiveness of the test.

III.4.1 Preliminary Investigations On Eastern Coals

A typical set of data, obtained using coals of different degrees of oxidation, is presented in Figure 28. These were then used to determine the equilibrium weight gain at infinite time (Figure 29). Corrections for the weight gain, caused by the imbibition of liquid into the filter paper used to cover the screen, was allowed for.

Variation of this parameter as a function of the extent of surface oxidation is presented in Figure 30. The results obtained show great sensitivity to small degrees of oxidation, but contrary to previous findings a peak was observed with coal oxidized up to 72 hours.

To test the suitability of the liquid selected (25% by volume methanol) for the purpose of measuring wettability, a series of tests were conducted using various alcohol concentrations (Figure 31). These data confirm that large infusion weight gains can be obtained with 25% aqueous methanol solutions and that equilibrium values can be quickly reached. These data will also help in elucidating the mechanism by which adsorption affects wettability.

A total of 48 experiments were conducted on eastern coals using this technique.

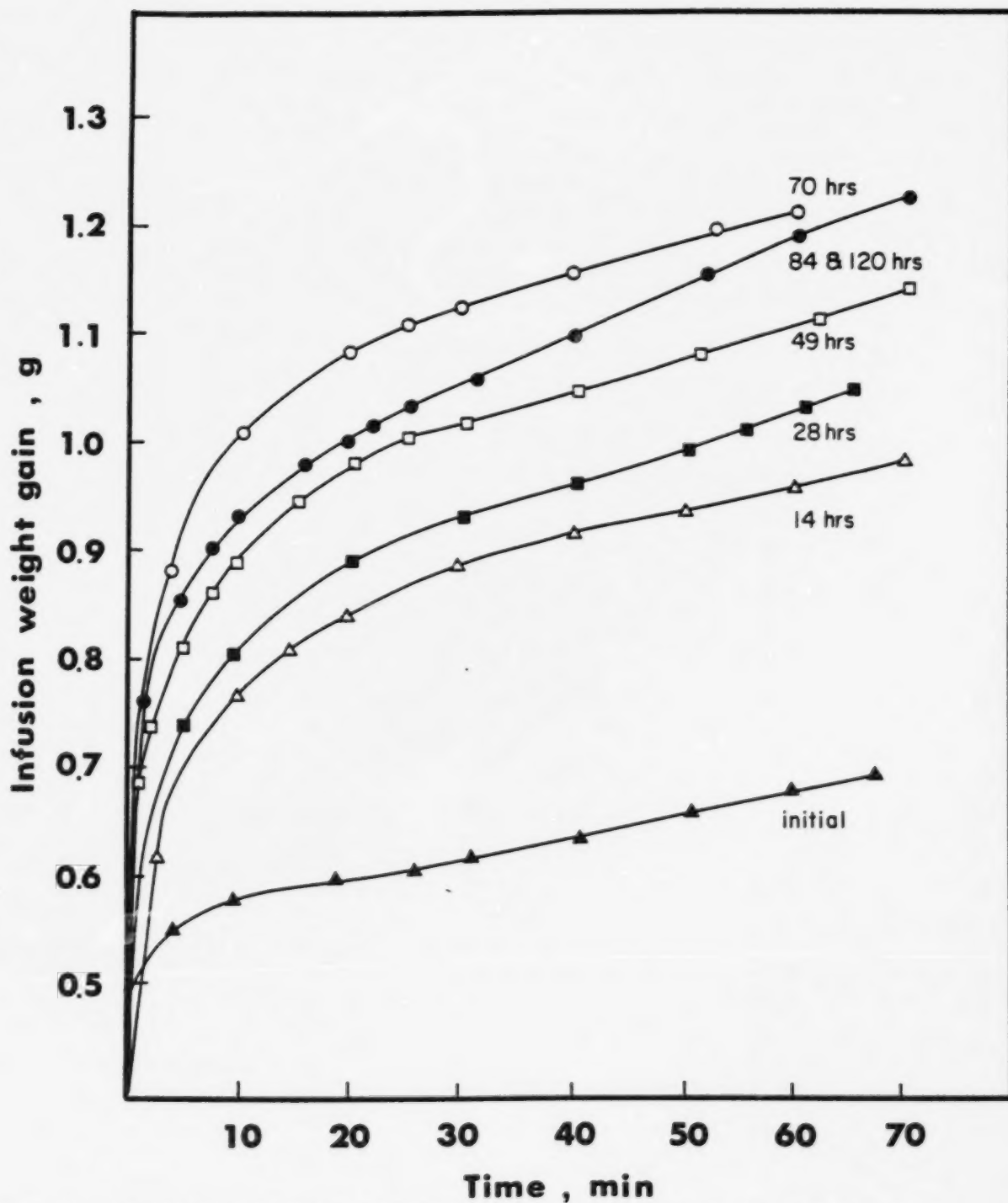


Figure 28 Infusion Weight Gains of 25% Methanol for 2 Grams of -200 +270 Mesh Size Prince Mine Coal Oxidized

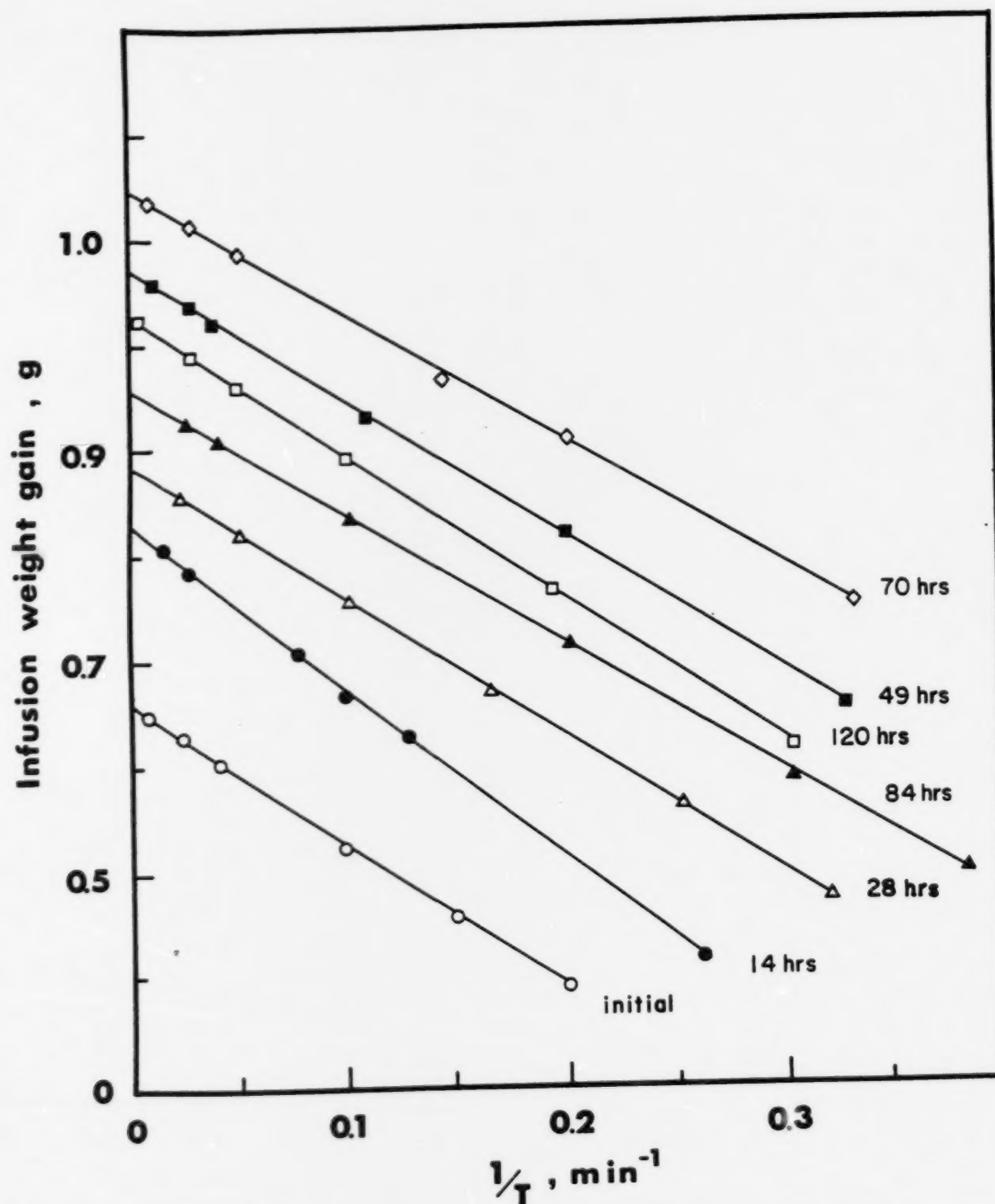


Figure 29 Infusion Weight Gains of 25% Methanol for 2 Grams of Prince Mine Coal (Data Taken From Figure 16)

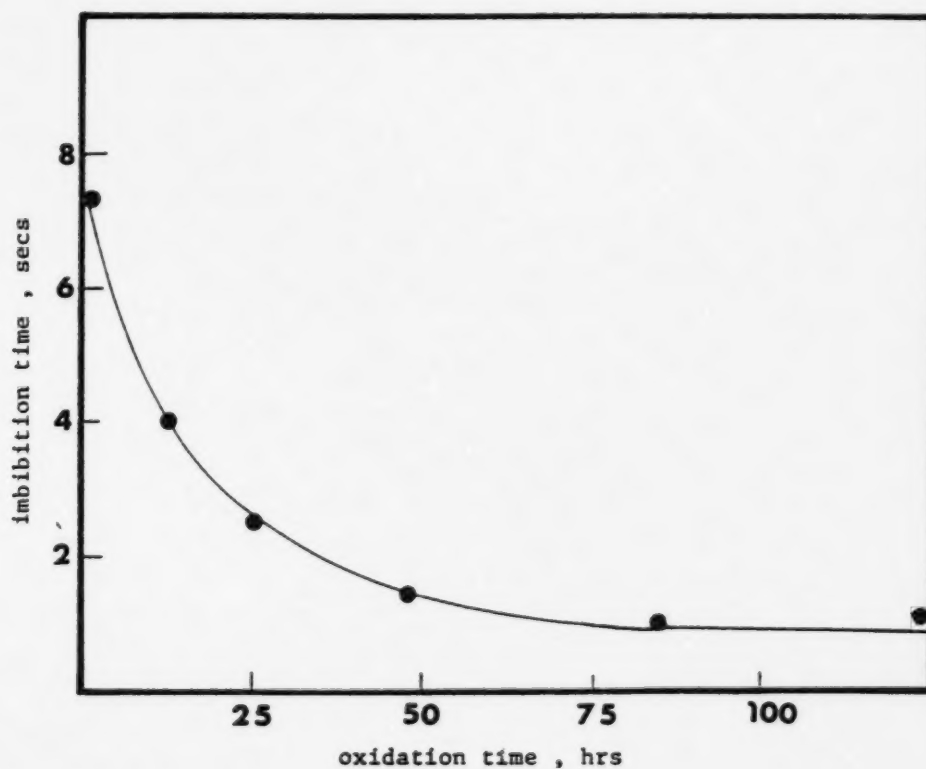


Figure 30 Effect of Surface Oxidation On Equilibrium Weight of Liquid Imbibed In A Bed of Compacted Coal (-200 +270 Mesh Prince Mine Coal Wetted By 25% Volume Aqueous Methanol Solutions)

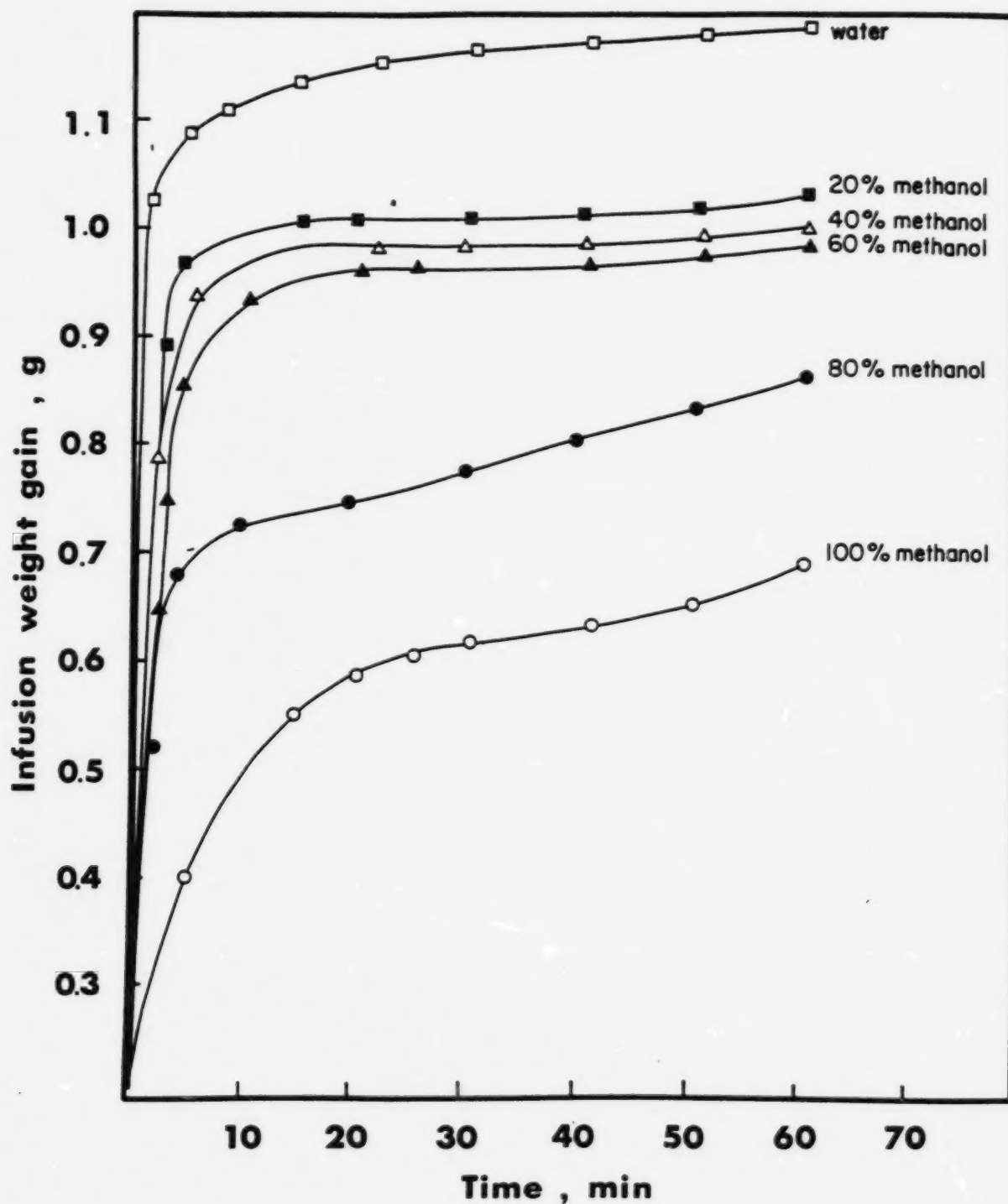


Figure 31 Variation of Infusion Weight Gains With Different Concentration of Methanol (2 Grams of Prince Mine Coal)

III.4.2 Evaluation of Reproducibility

The reproducibility of this technique was found to be affected by the condition of the surface of the coal and by how close the measurement is to the final equilibrium value (Table 16). The reproducibility is relatively low in the initial stages of measurement ($\pm 8-17\%$) and steadily improves as equilibrium conditions are approached ($\pm 2-5\%$). This improvement in reproducibility is brought about mainly by a reduction in the random error (). This parameter was also found to be affected by the composition of the liquid used in this testing, with a minimum observed at 40% and 80% volume aqueous methanol solution (Table 17).

TABLE 16 Effect of Coal Oxidation and Measurement Time of the
Reproducibility of Dynamic Penetration Measurements

Measurement Time (min)	No. of Replicates	Error = $\sqrt{n-1/X}$ (% age)					
		0 hrs	14 hrs	28 hrs	49 hrs	84 hrs	120 hrs
1	4	12.4	13.0	17.2	12.1	9.9	8.1
2	4	8.2	9.6	11.6	12.0	7.8	6.5
3	4	8.0	8.5	11.0	10.3	7.8	4.2
4	4	6.1	8.5	10.4	6.1	7.8	3.4
10	4	5.2	6.6	4.4	3.9	6.1	3.6
15	4	5.0	6.0	4.2	4.0	4.5	2.1
30	4	4.7	5.4	4.1	2.3	3.8	1.9
60	4	4.2	4.9	2.7	2.2	3.9	2.5

* 25% vol. aqueous methanol solution.

Keeping in mind that this technique ultimately yields the equilibrium weight gain (at Time = ∞), the reproducibility of this significant parameter is better than $\pm 4\%$.

TABLE 17 Effect of Wetting Liquid Composition on the
Reproducibility of Dynamic Penetration test

Measurement Time (min)	No. of Replicates	Error ($\sqrt{n-1/\bar{X}}$), % age	
		40%	80%
1	4	10.2	4.8
2	4	9.1	3.7
3	4	8.1	3.7
5	4	1.8	3.9
10	4	1.2	3.1
20	4	1.2	2.5
30	4	1.2	2.5
40	4	1.4	2.3
50	4	1.2	2.1

*-200 +270 mesh unoxidized Prince Mine coal wetted by aqueous methanol solutions

III.4.3 Application To Western Coal Samples

Infusion weight gain tests were conducted using 3 gm samples of the -200 +270 mesh fraction of all Western coal samples. Three liquids were tested (namely: water, n-heptane and 25% aq. Methanol) but the data obtained with water were unsatisfactory. With the exception of sample No. 5, negative values were obtained, which suggests that water is incapable of penetrating the capillary structure of hydrophobic coals.

The data obtained using hydrophobic and hydrophillic wetting liquids are presented in Figures 32 to 43 from which it is evident that the behaviour of the six Western samples is radically different from that of the Eastern coals tested. Two distinct regions can be clearly identified in the case of Western

coals. At short contact times (less than 12 minutes) liquid imbibition is mainly controlled by the liquid rising in the inter-particle capillaries formed in the compacted bed. Further imbibition taking place at longer contact times could be the result of liquid penetration into the macro and micro pores present in the coal particles, or a by-product of surface conditioning taking place as the liquid adsorbs on the surface of the coal. At present it is difficult to discern which mechanism is responsible for the second stage of imbibition, and emphasis was, therefore, placed on the first stage since it is thought to represent the surface component that plays an important role in beneficiation. The ultimate weight gain, obtained by extrapolating the data of the first stage of liquid imbibition, are listed in Table 18.

TABLE 18 Maximum Infusion Weight Gains for Western Coal Samples

EMR Sample	Wetting Liquid	
	25% Aq. MeOH	n- heptane
1	0.28	1.37
2	0.52	1.55
3	1.30	1.21
4	0.17	0.20
5	1.40	0.93
6	0.80	0.75

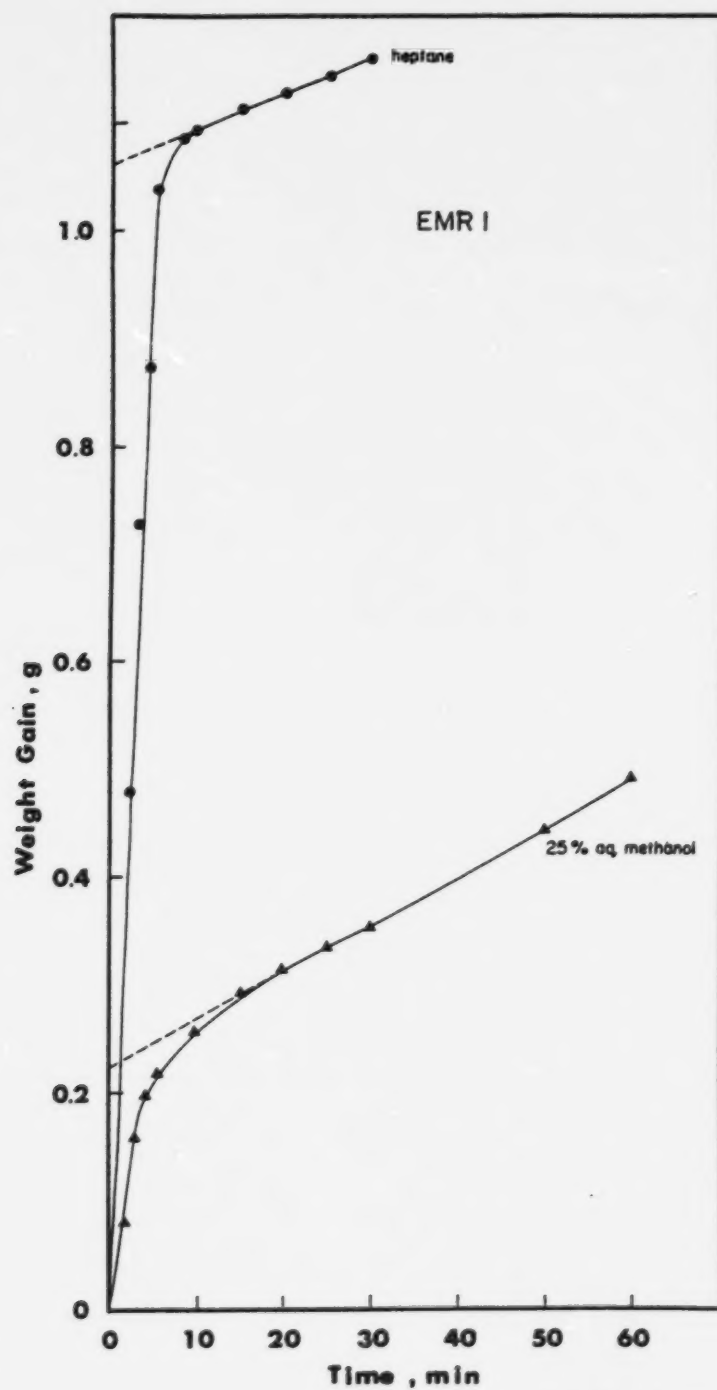


Figure 32 Weight Gain Data For EMR Sample NO. 1

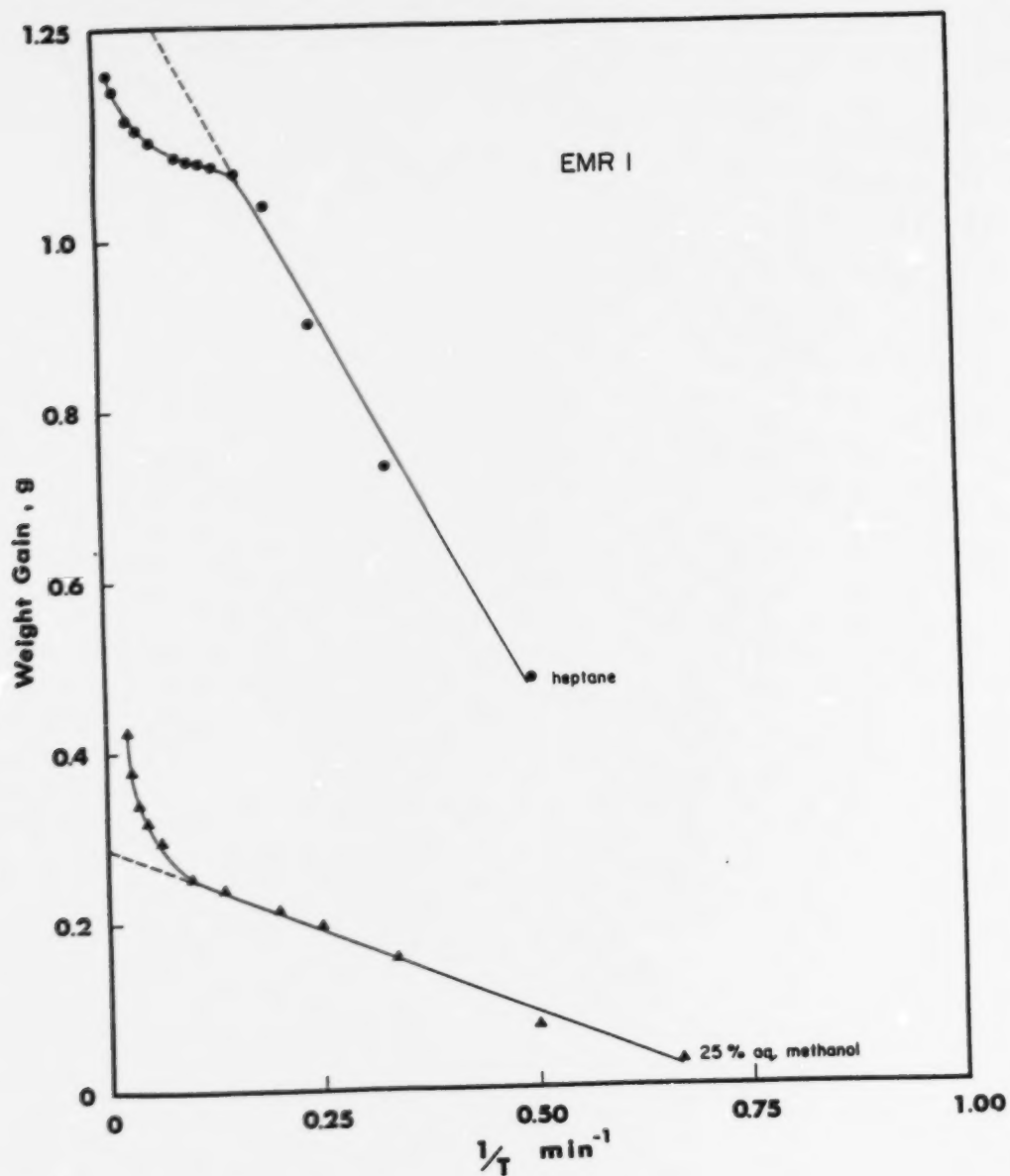


Figure 33 Effect of Contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 1)

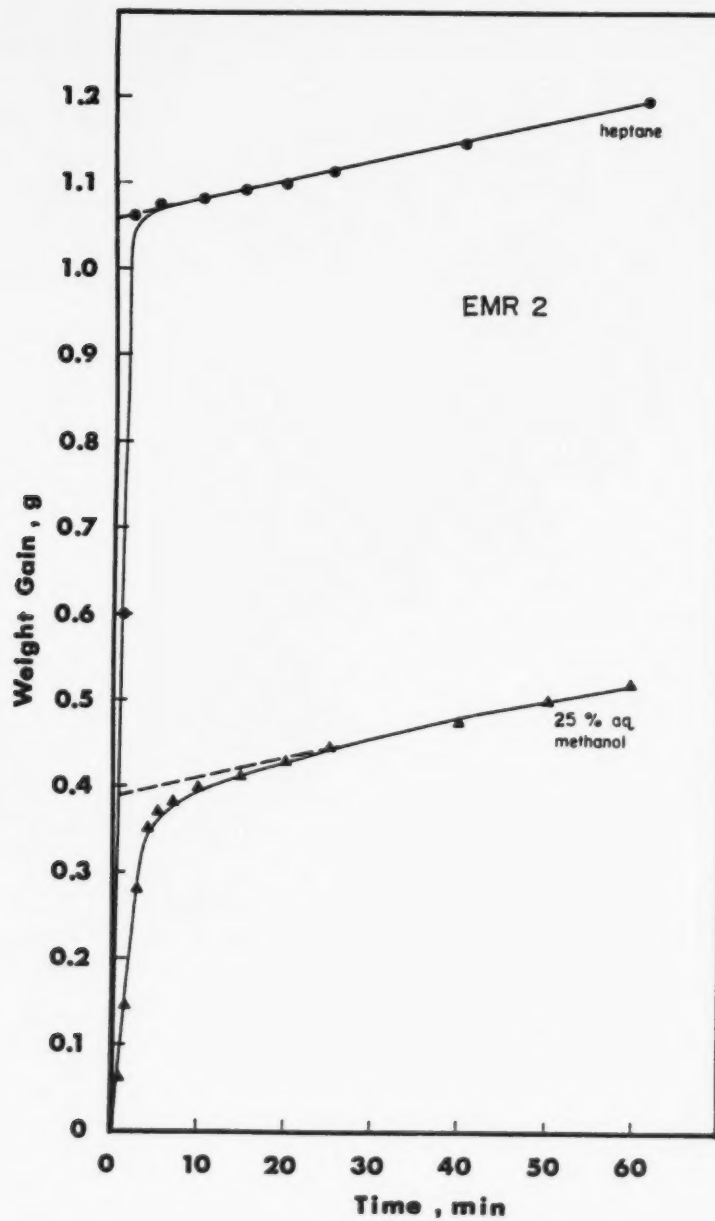


Figure 34 Weight Gain Data For EMR Sample No. 2

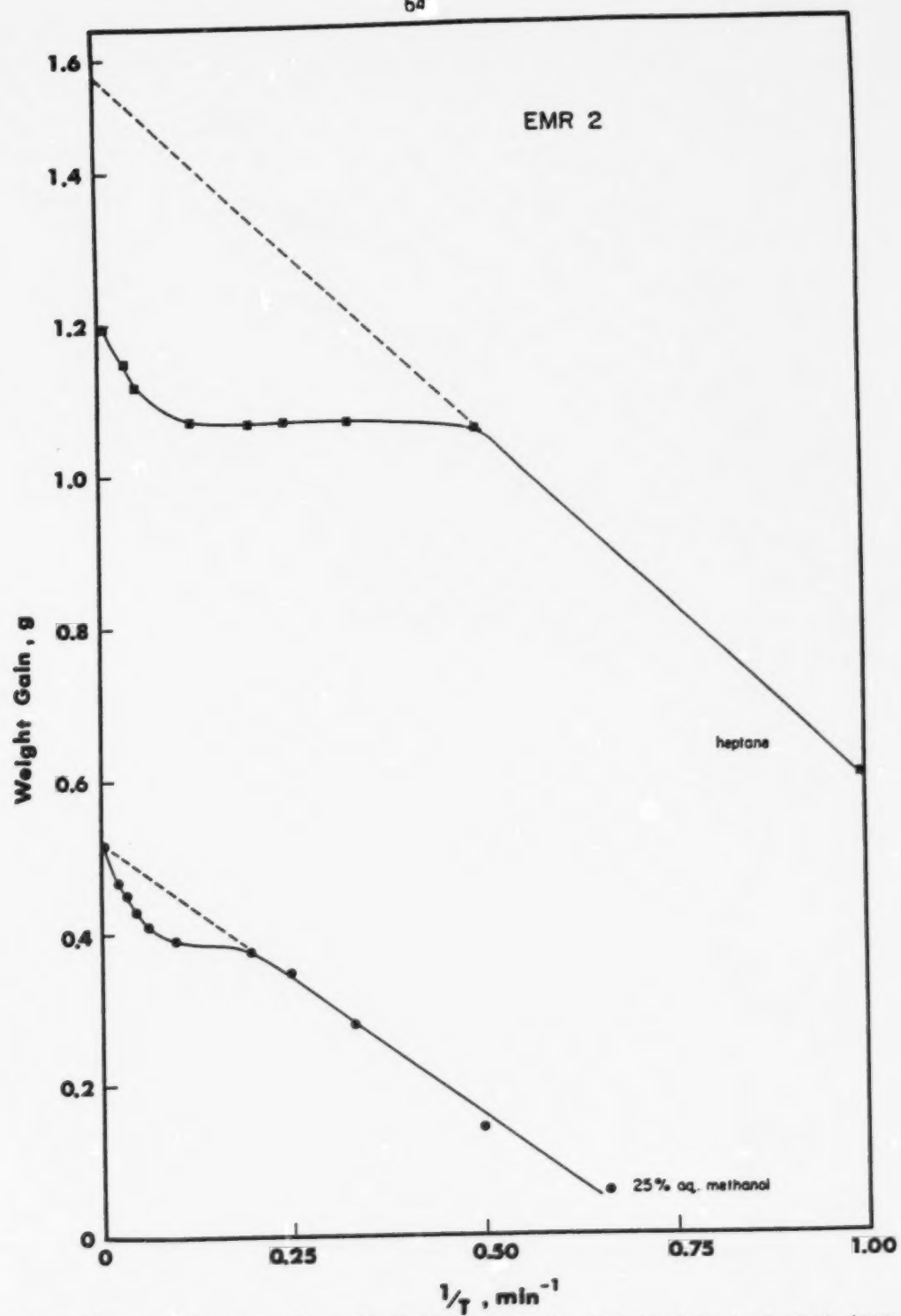


Figure 35 Effect of Contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 2)

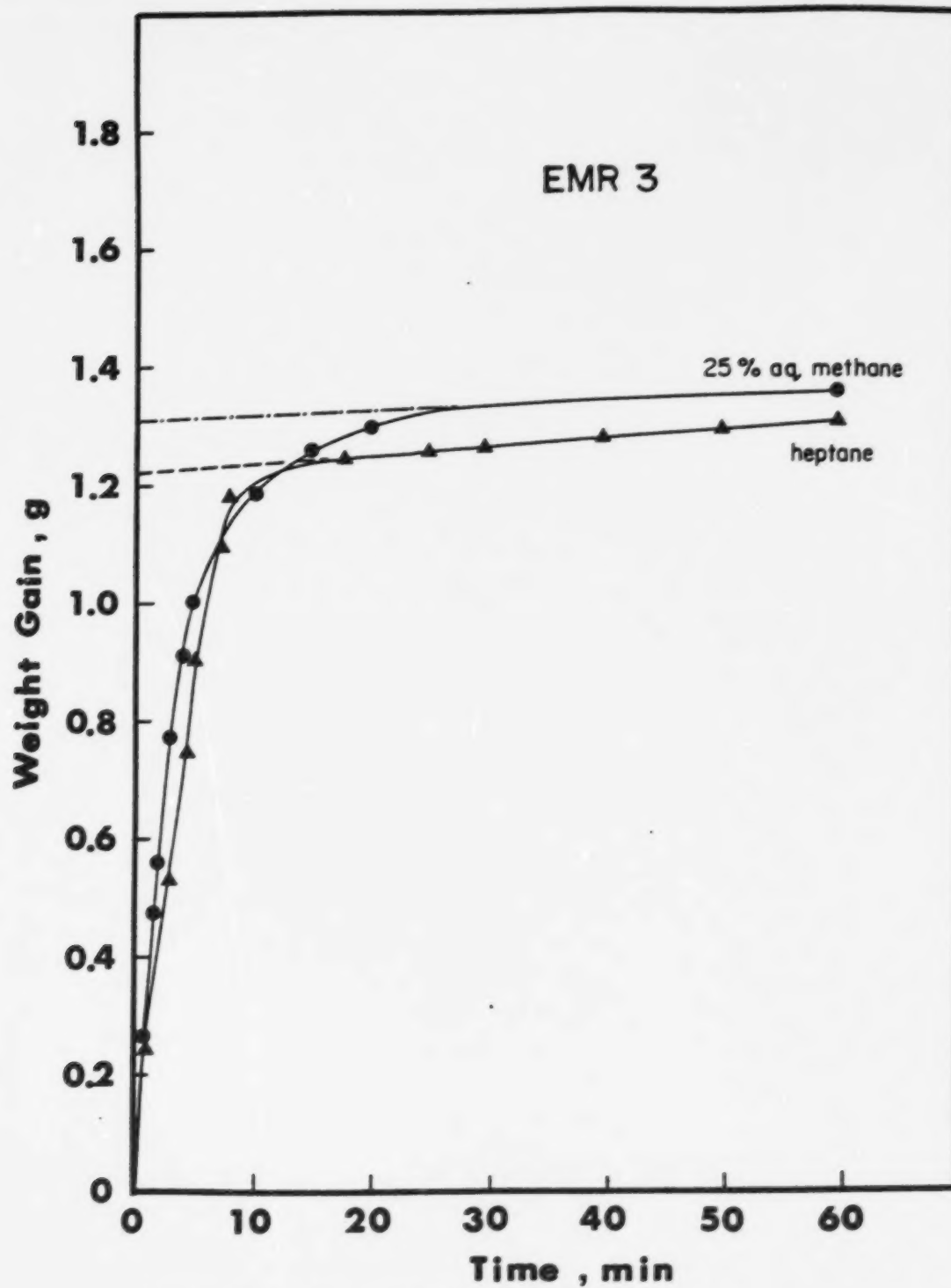


Figure 36 Weight Gain Data For EMR Sample No. 3

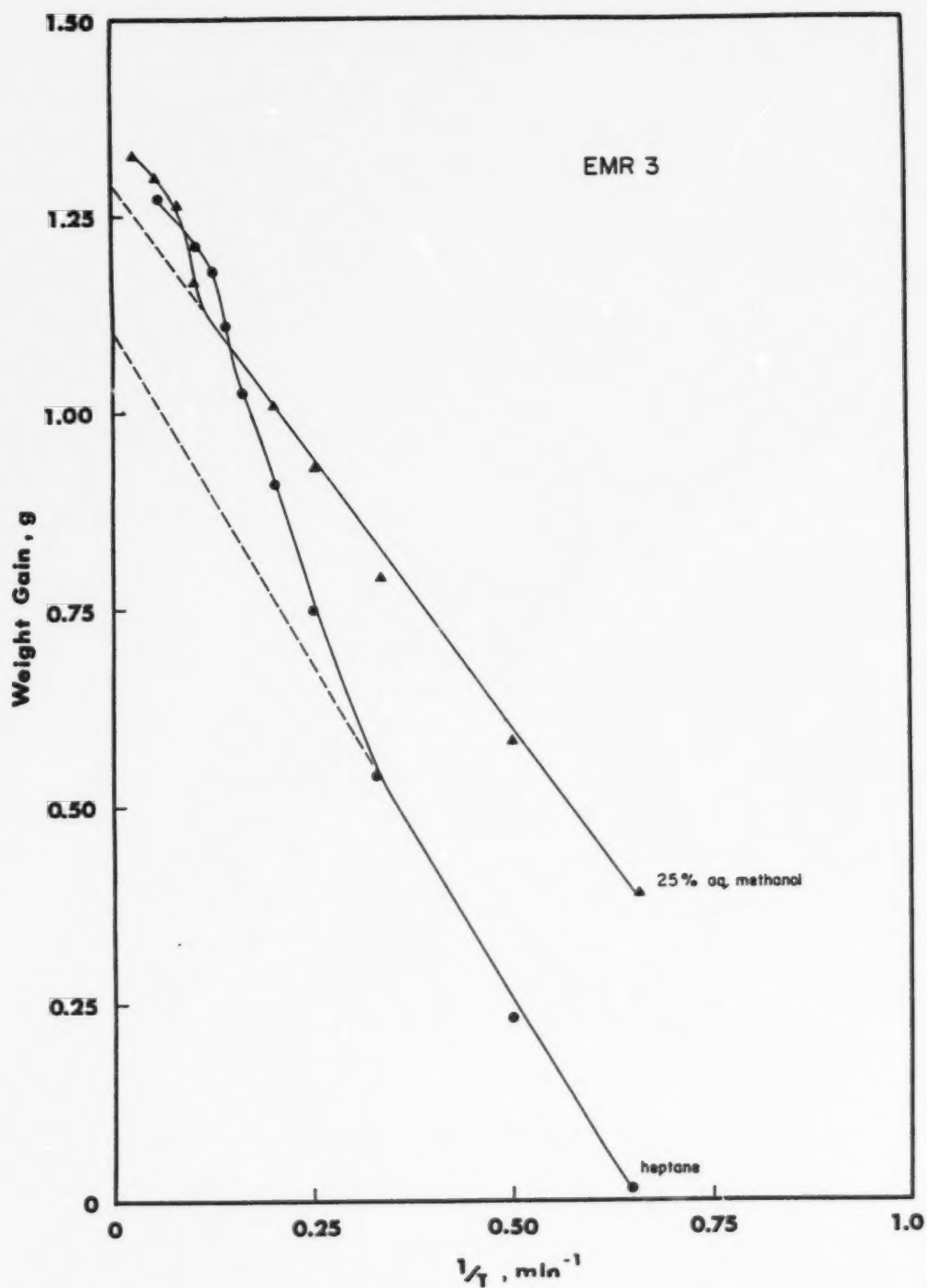


Figure 37 Effect of Contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 3)

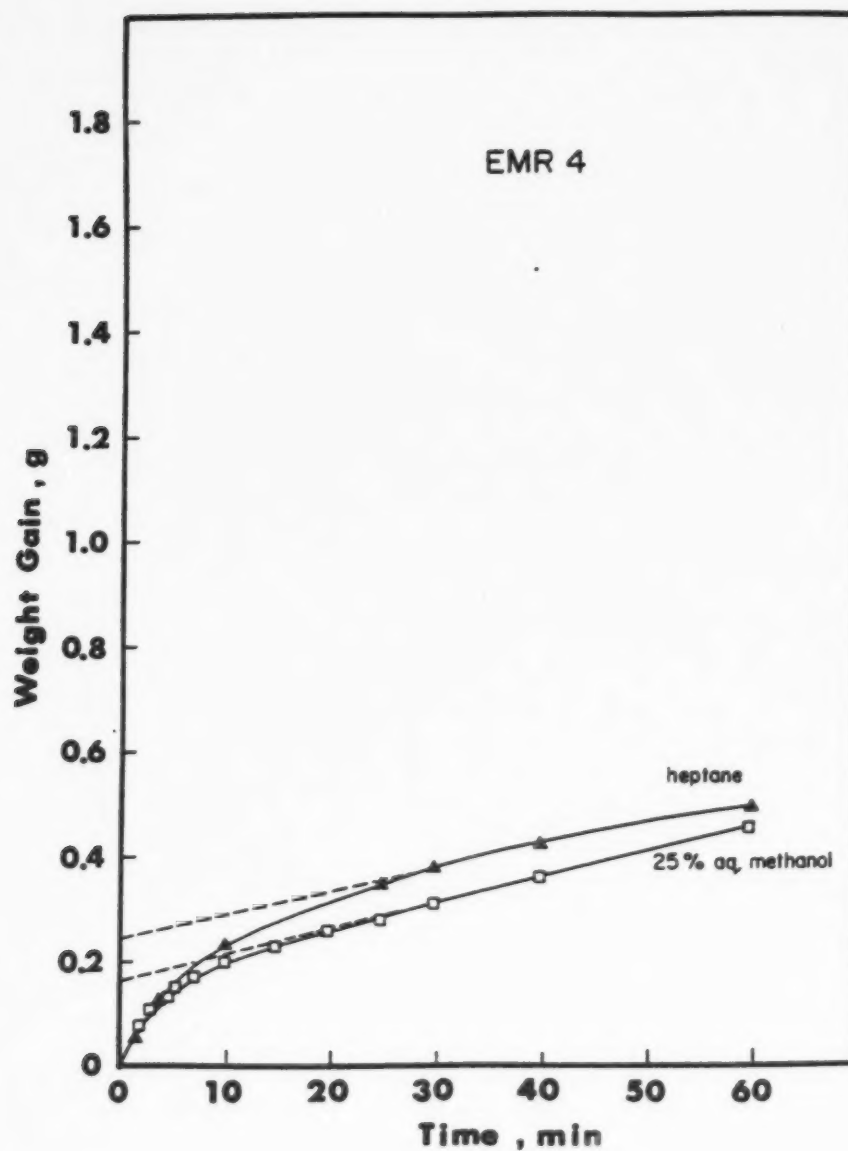


Figure 38 Weight Gain Data For EMR Sample No. 4

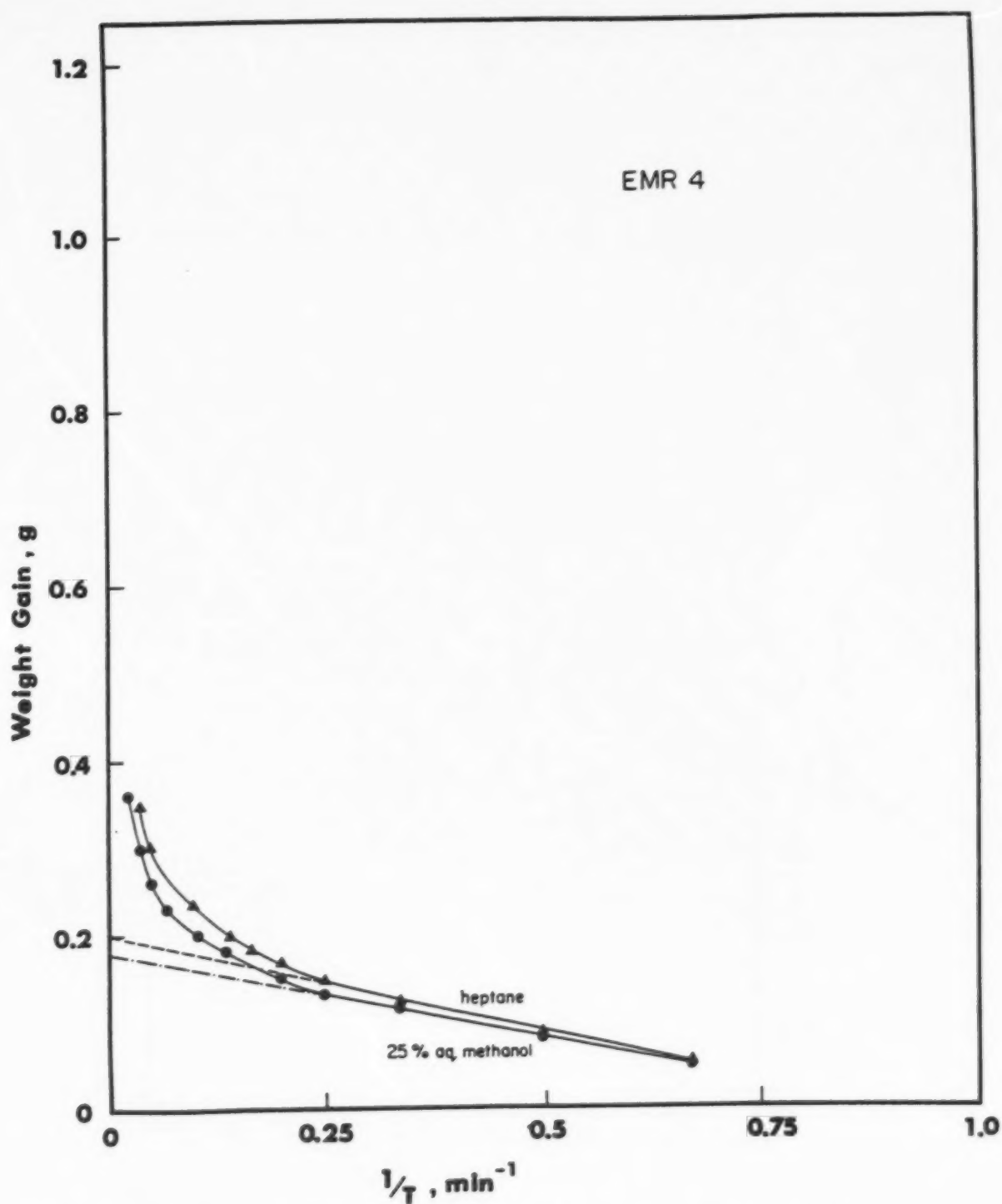


Figure 39 Effect of contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 4)

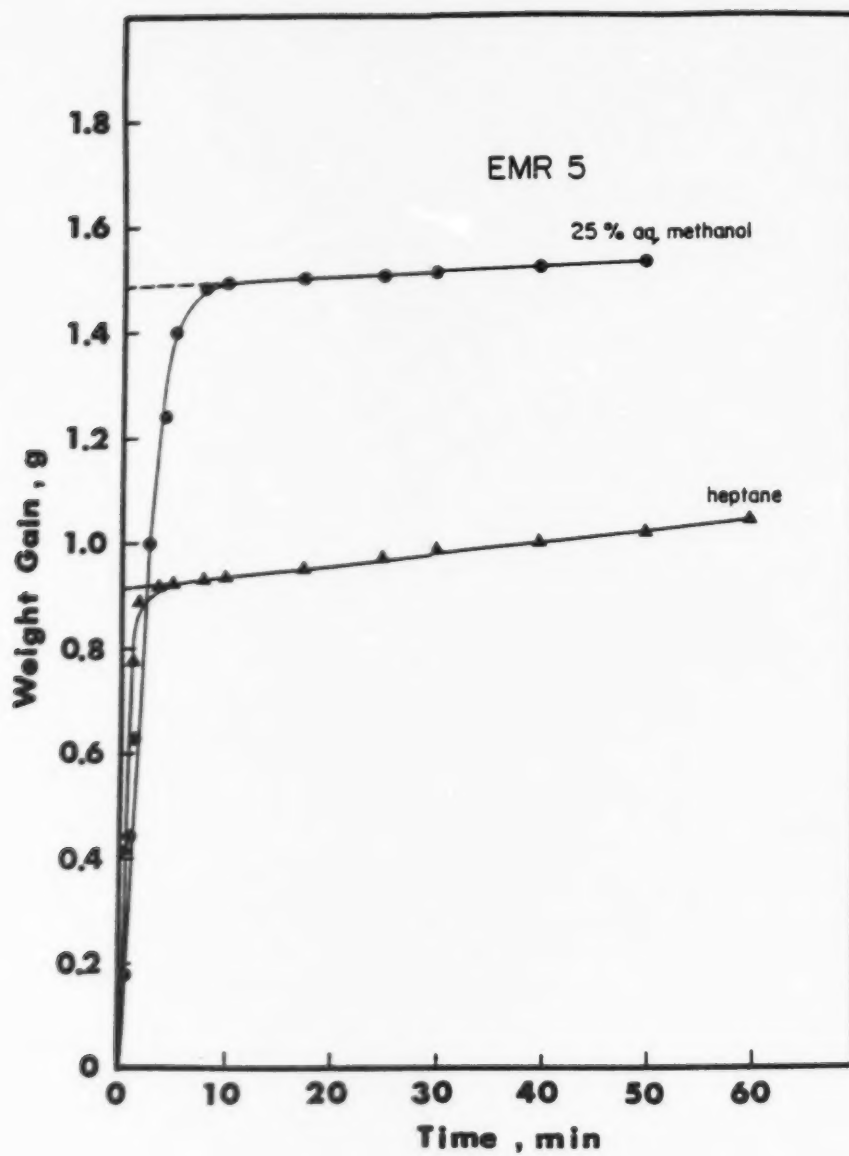


Figure 40 Weight Gain Data For EMR Sample No. 5

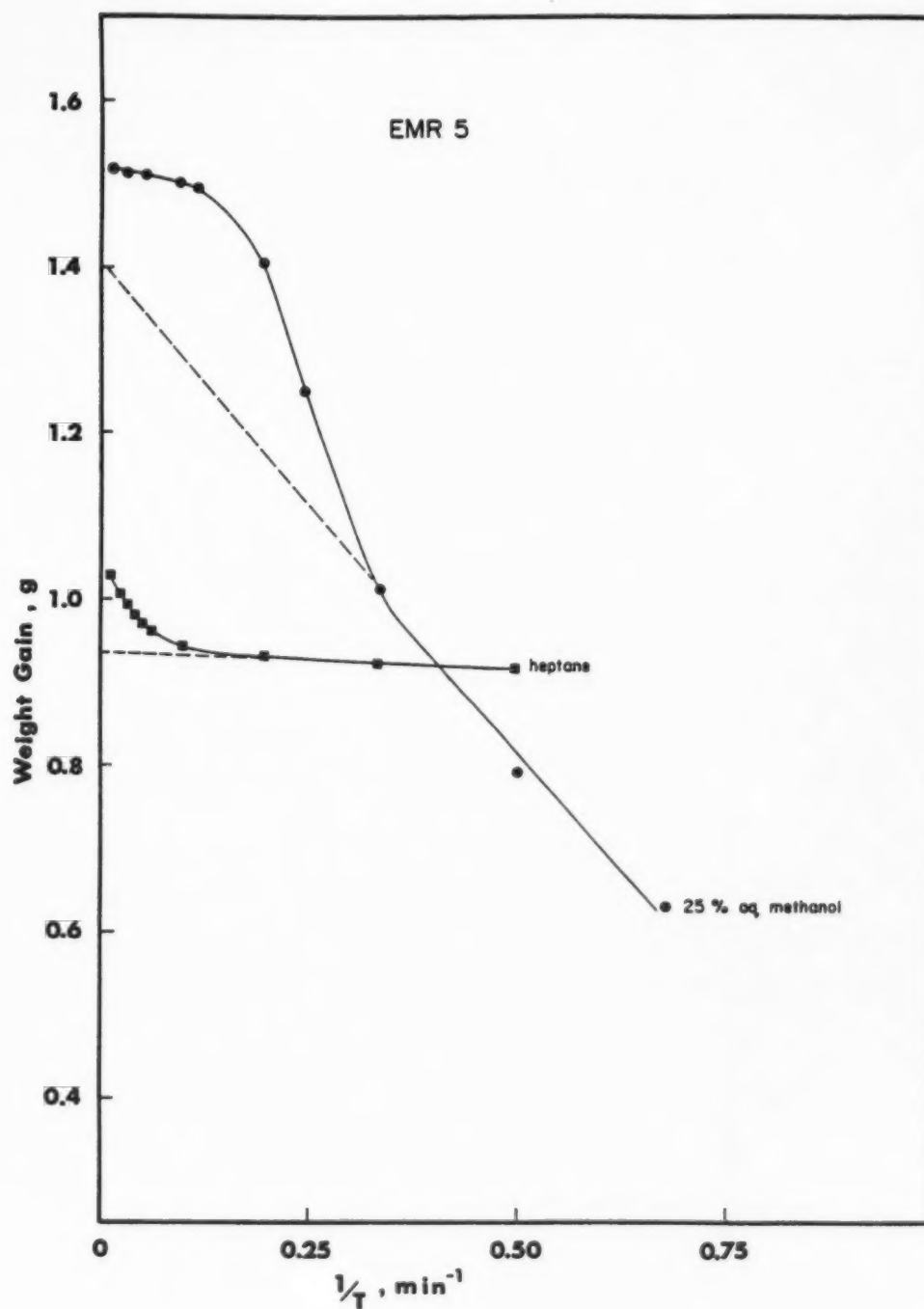


Figure 41 Effect of Contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 5)

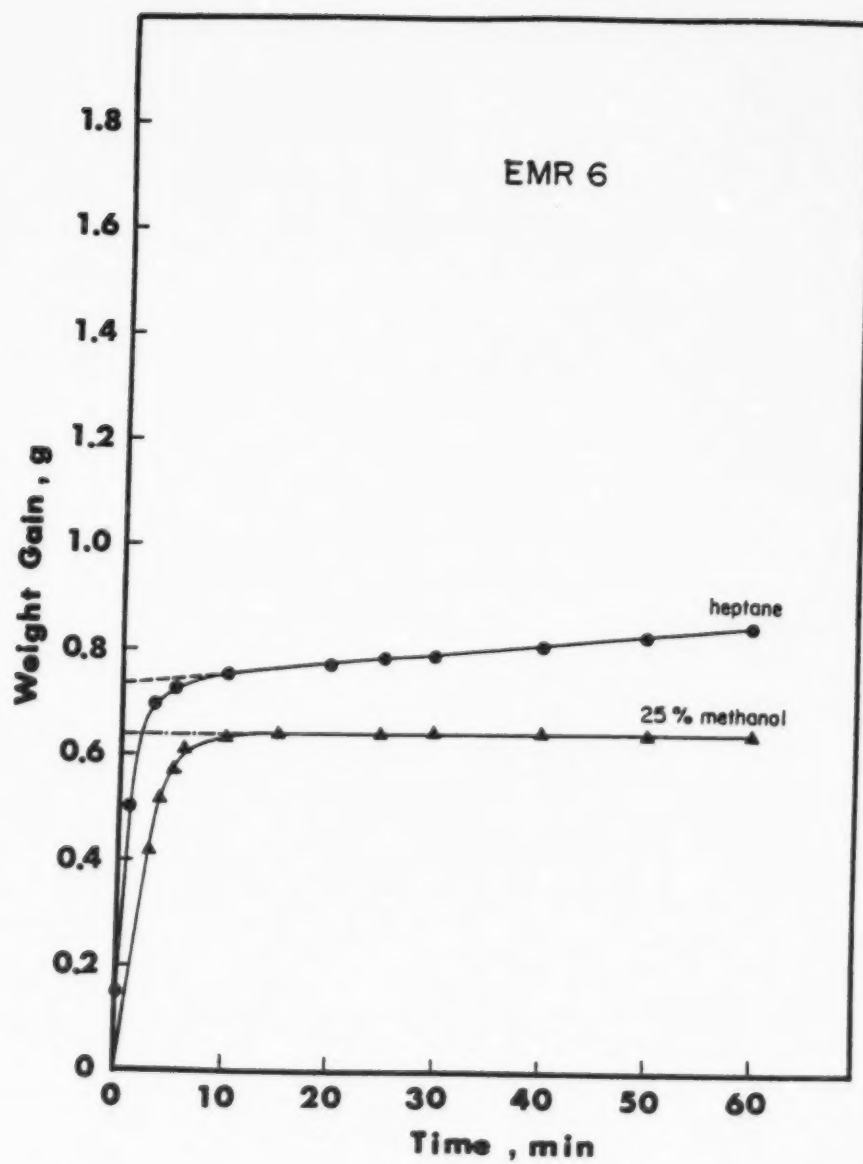


Figure 42 Weight Gain Data For EMR Sample No. 6

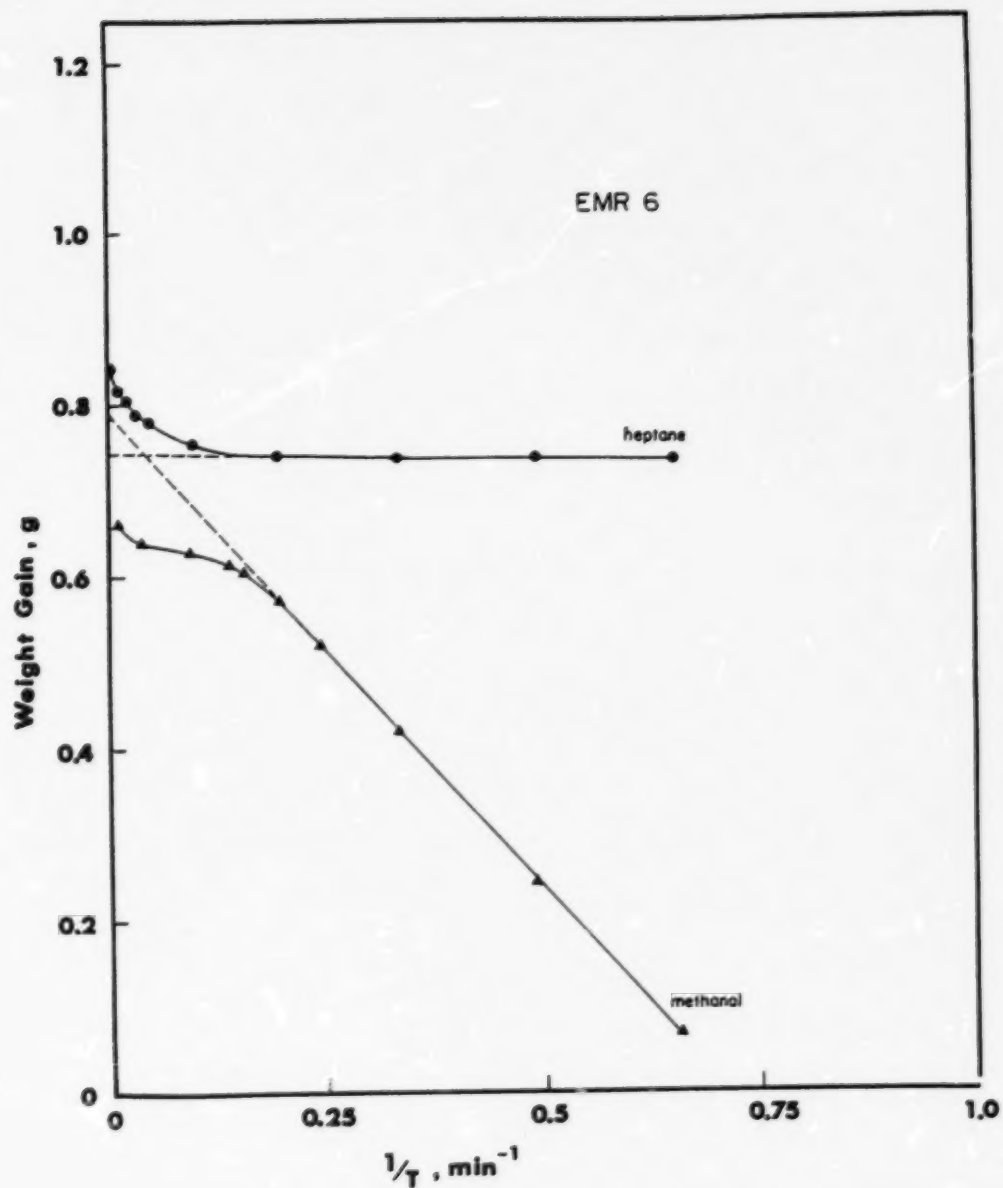


Figure 43 Effect of Contact Time On Weight Gain In A Packed Bed of Coal (EMR Sample No. 6)

III.5 Minimum Pressure Needed For the Formation of a Bubble Under a Wetted Bed

These measurements differ from previous ones in that they are dependent on the receding angle of contact. However, they share the common characteristic of being dependent on the degree of bed compaction. By adopting ASTM Compaction techniques a reproducibility of $\pm 10\%$ was obtained when dry coal was compacted while the reproducibility was slightly less ($\pm 7.0\%$) when wet coal was compacted. A blank pressure drop of 18 mm water was subtracted from all data to account for the liquid level above the point at which bubbles emerge as well as the pressure needed for their formation in an empty sample holder.

III.5.1 Preliminary Investigation of Eastern Coals

The data obtained at various degrees of oxidation are reported in Figure 44 from which a minimum was observed to occur after approximately 40 hours of oxidation.

A total of 168 experiments were conducted on Eastern coals using this technique and each data point represents the range of triplicate testing.

III.5.2 Evaluation of Reproducibility

The reproducibility of this technique is strongly affected by the reproducibility of compacting the bed tested. However, excellent average reproducibility (less than $\pm 5\%$) was ultimately achieved after compacting the sample in accordance with ASTM standard (Table 19).

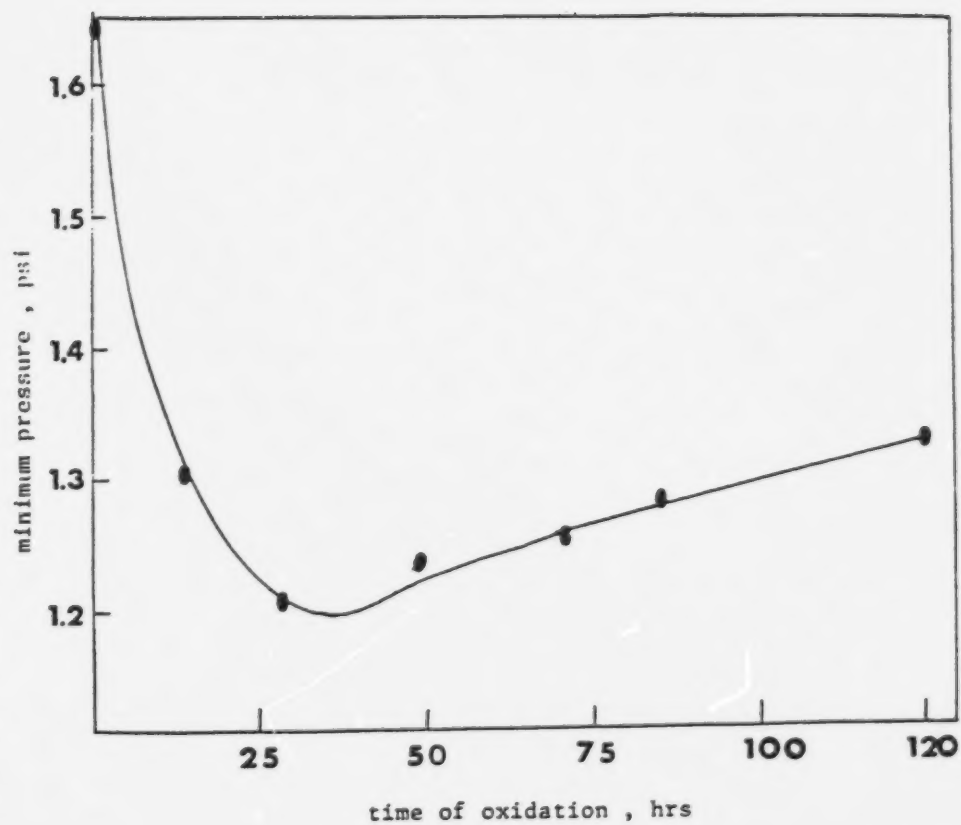


Figure 44 Effect of the Degree of Surface Oxidation On the Minimum Pressure Needed For the Formation of A Bubble (-200 +270 mesh Prince Mine Coal Wetted By 25% Volume Aqueous Methanol Solution)

TABLE 19 Effect of Oxidation Time on the Reproducibility
of Bubble-Pressure Technique*

Oxidation Time (hr)	No. of Replicates	Error ($\bar{n}-1/X$), % age	
		25%	20%
0	12	4.3	8.0
14	12	2.6	5.2
28	12	4.7	7.0
49	12	6.7	10.0
70	12	5.5	9.1
84	12	3.1	4.2
120	12	2.2	5.1

*-200 +270 mesh coal samples wetted by aqueous methanol solutions

III.5.3 Application To Western Coal Samples

The results obtained using this technique in conjunction with the Western coal samples are depicted in Figure 45 from which it is evident that higher pressures are needed to overcome the stronger affinity between aqueous methanol solutions and coals of progressively increasing hydrophobicity.

To determine whether coal surfaces are affected by prolonged contact with the wetting liquids, the minimum bubble pressure was determined after contacting the sample with the liquid for a period of 2 and 30 minutes respectively. The results obtained are listed in Table 20; from which it becomes evident that with the exception of coal samples No. 2 and 6, the surfaces were rendered slightly more hydrophobic upon prolonged contact with aqueous methanol solutions. Significant improvement in the reproducibility of the test was also observed to take place upon prolonged contact with the solution. These

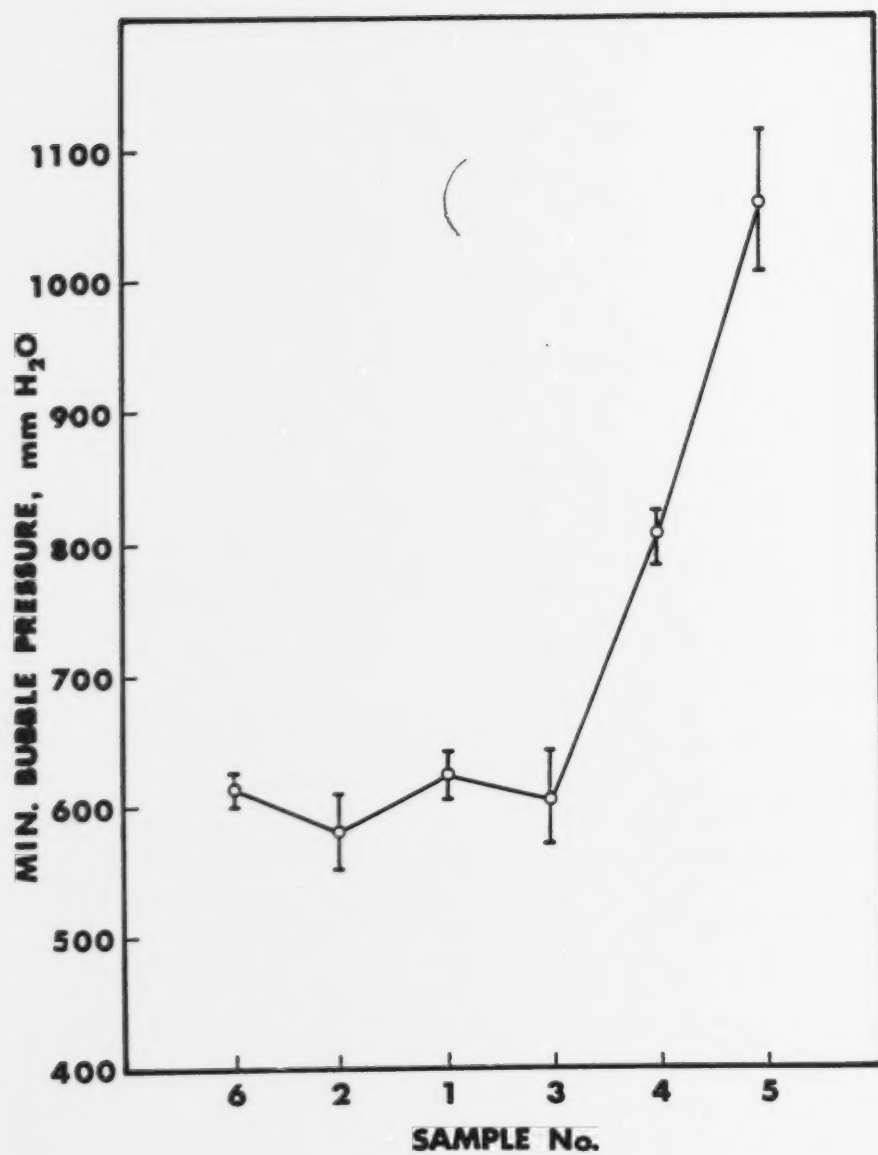


Figure 45 Effect of Coal Hydrophobicity On the Minimum Pressure Required To Form A Bubble

observations suggest that methanol and/or water tends to adsorb on some of the more active sites, with consequent alteration of the average surface characteristics and a definite reduction in the extent of surface nonhomogeneity.

TABLE 20 Results of Minimum-Bubble-Pressure Measurements
When Applied To Western Coals

Sample No.	No. of Replicates	Min. Bubble Pressure*	/x, %	Min. Bubble	/x, % Pressure
1	4	687	11.6	623	2.5
2	3	529	15.3	574	6.3
3	3	684	5.2	607	6.6
4	3	807	2.5	800	2.2
5	3	1089	11.2	1053	7.9
6	3	567	10.4	610	1.5

*in mm of water head

III.6 Heat of Wetting

This technique is one of the first to be used for investigating the internal surface characteristics of coal [38-46]. A variety of wetting liquids have been used by previous investigators but methanol became the preferred one because of the relatively high value of its heat of wetting and the speed at which it is delivered. Thus, for example it is estimated that 95% of the heat is released within 10 minutes and 99% within 25 minutes [39].

When methanol, or any other liquid, penetrates coal it begins to swell. This process is endothermic and is counteracted by the exothermic interactions between methanol and the oxygen-containing active sites present on the

surface of the coal [43,44]. The heat of wetting is, therefore, the net resultant of the energy being consumed by the former, and that released by the latter.

III.6.1 Preliminary Investigations of Eastern Coals

The heat of wetting for progressively oxidized coal is depicted in Figure 46. These data were corrected for the mechanical energy stemming from the mechanical breakage of the evacuated glass ampoules. No allowance for the variation of swelling was included since this parameter is considered to be one of the characteristics affected by the liquid/solid surface-interactions and is inherently included in the H value.

The heat of immersion, for both methanol and ethanol, was found to increase with increasing levels of oxidation, with the former being slightly higher than the latter. However, whereas the methanol data seem to reach a plateau after 84 hours of oxidation, the ethanol data steadily increase with increasing level of oxidation.

III.6.2 Evaluation of Reproducibility

The reproducibility of heat of wetting measurement was found to improve with increasing degree of coal oxidation (Table 21). This improvement stems mainly from the increase in the magnitude of the heat of wetting, measured at an almost constant value of the random error. Similarly, the slightly lower reproducibility observed with ethanol can be attributed to its lower heat of wetting since the standard deviation of the two alcohols is almost identical.

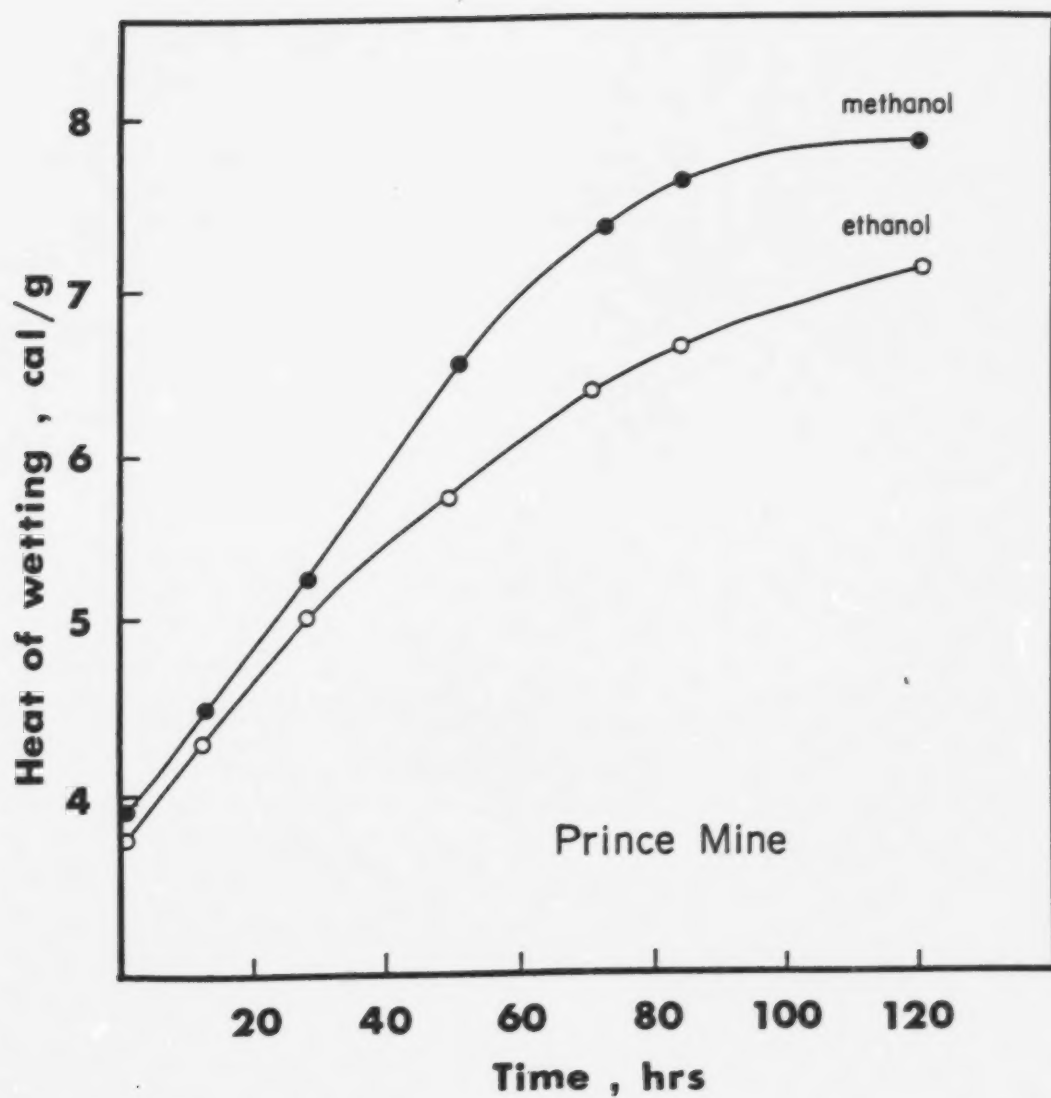


Fig.46 Effect of the degree of surface oxidation on the heat of immersion in alcohols

●--Methanol o--Ethanol
(error range within symbol)

TABLE 21 Effect of Coal Oxidation On the Reproducibility
of Heat of Wetting Measurements

Oxidation Time	No. of Replicates	Error ($(n-1/X)$ % age	
		Methanol	Ethanol
0	3	5	5.9
14	3	3.2	4.4
28	3	2.7	3.4
49	3	2.2	2.5
70	3	1.6	2.3
84	3	2.8	2.1
120	3	1.8	2.0

III.6.3 Application To Western Coal Samples

The data obtained while testing the six Western coal samples provided by CANMET, are shown in Figure 47, from which it is evident that the heat of wetting by methanol increases with increasing hydrophobicity of the coal. However, when these measurements were normalized with respect to the BET surface area (as determined from methanol adsorption) in order to yield the specific heat of wetting, the resulting values were found to be almost constant regardless of the rank or state of oxidation of the coal (Figure 48). These values are very close to those reported by Magg [41] and suggests that coals formed, or stored for extremely long periods at environmental conditions, have similar average energies of interactions between methanol and the various oxygen-containing functional groups present on the surface of the coal. Weathering and coalification apparently does not affect this equilibrium distribution of active sites, but rather its overall surface concentration as well as the pore structure of the coal. On the other hand, oxidation

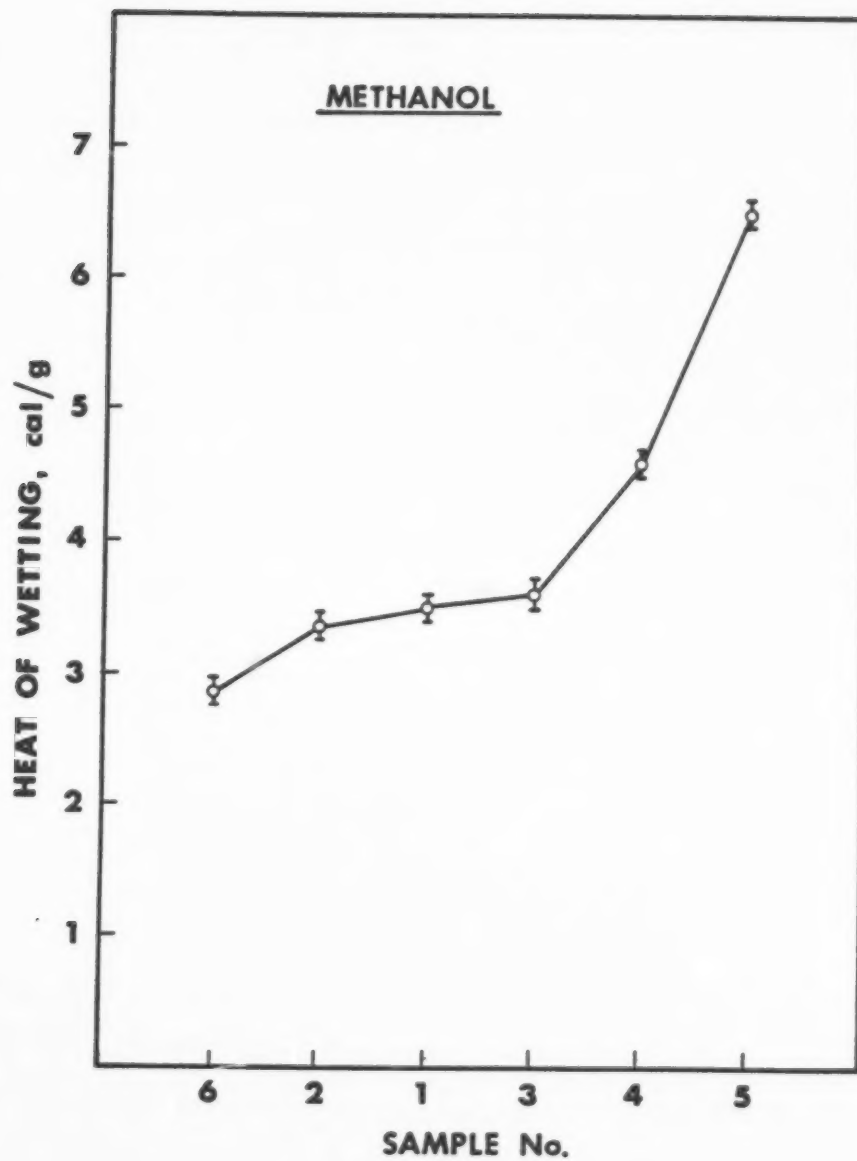


Figure 47 Effect of the Coals' Hydrophobicity On the Heat of Wetting By Methanol

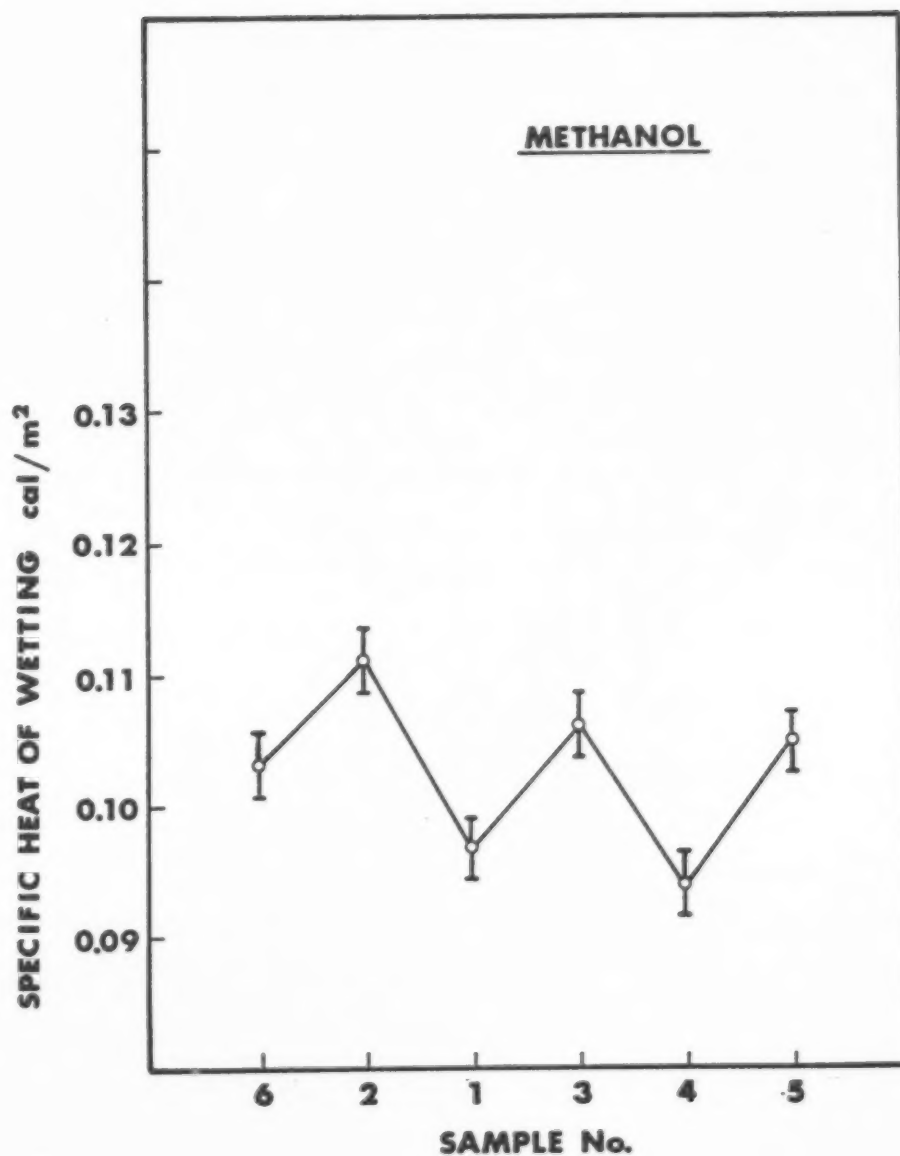


Figure 48 Effect of Coal's Surface Characteristics On Its Specific Heat of Wetting By Methanol (BET Surface Area As Determined By Methanol Adsorption)

of coal at higher temperatures results in the formation of active sites with higher energy of interaction (Figure 49). It appears, however, that an equilibrium situation is approached after prolonged oxidation times.

The reduced energy of interaction resulting from the wetting of Western coals by methanol has resulted in slightly lower reproducibility, as shown in Table 22.

TABLE 22 Reproducibility of Heat-of-Wetting Measurements (Western Coals)

EMR Sample No.	No. of Replicates	Error $\sigma_{n-1}/\bar{X}$, %
1	3	6.1
2	3	5.9
3	3	6.2
4	3	6.0
5	4	4.3
6	3	5.8

III.7 Vapour Adsorption On the Surface of Coal

In this method the quantity of vapour sorbed at constant temperature is determined at different pressures, and the resultant data usually utilized for the determination of the internal surface area and pore structure. This approach has been extensively applied to various coals [47-77] but data interpretation has generally suffered from the tendency to treat coal as a uniform surface rather than that of a highly heterogeneous material. Thus, for example, the same coal was found to have radically different internal surface areas depending on the type of adsorbate used. Such difficulties can,

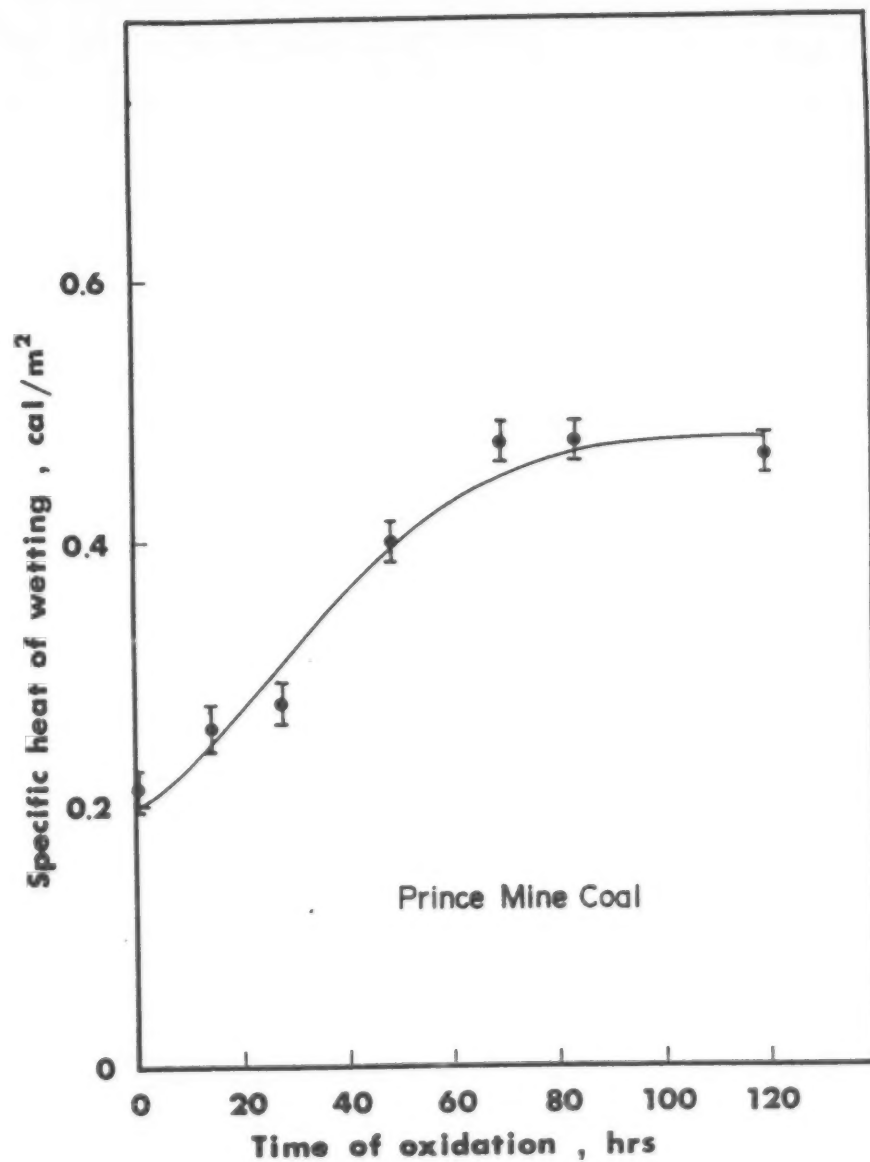


Figure 49 Effect of Coal Oxidation At 100°C On the Specific Heat of Wetting By Methanol

however, be easily reconciled if coal is treated as a heterogeneous surface with a spectrum of active sites to which various adsorbates could have different affinities.

The dynamic adsorption technique was used for evaluating the surface characteristics of various coal samples and the data were evaluated as described in the attached document.

III.7.1 Preliminary Investigations Using Eastern Coals

The surface area and pore structure of various coals was determined using the dynamic adsorption technique. Measurements were conducted in triplicates to evaluate the reproducibility of the technique and its variation as a function of adsorbate type and the extent of coal oxidation.

Two adsorbates were tested at room temperature (namely methanol and water vapors). Benzene isotherms were evaluated at 25 and 100°C. Typical examples are shown in Figures 50 to 55, and the initial parts of these isotherms ($P/P_0 < 0.35$) were used to evaluate the BET surface areas. The surface areas obtained for several Maritime coals is shown in Figure 56 while the effect of coal oxidation on the BET values is presented in Table 23.

The data shown in Figure 56, and those listed in Table 23, clearly indicate the errors introduced when coal is treated as uniform surface. The adsorption results are, therefore, more appropriately presented as the number of active sites interacting with the particular adsorbates (Tables 24 and 25).

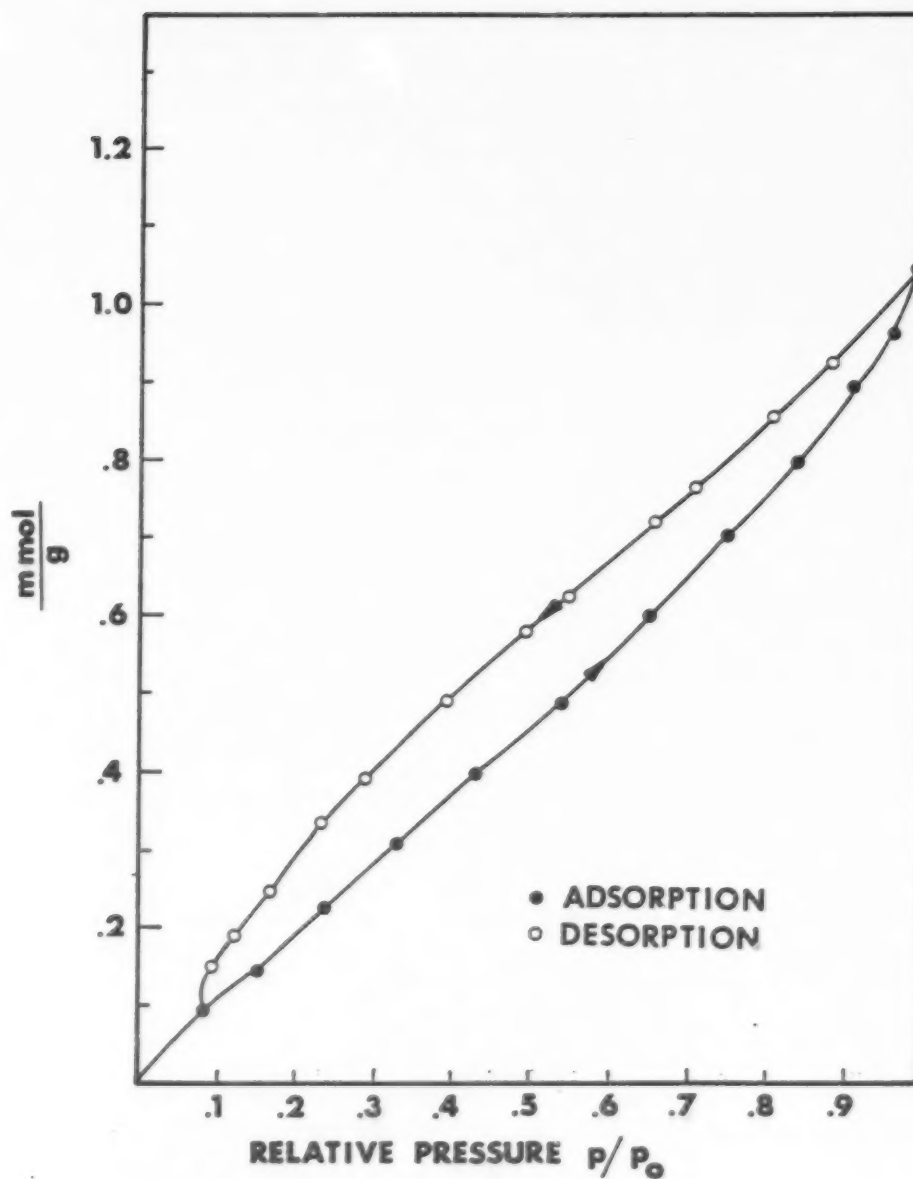


Figure 50 Typical adsorption & desorption isotherms, as determined by the dynamic technique (Methanol Adsorption On EMR1 Coals @ 25°C)

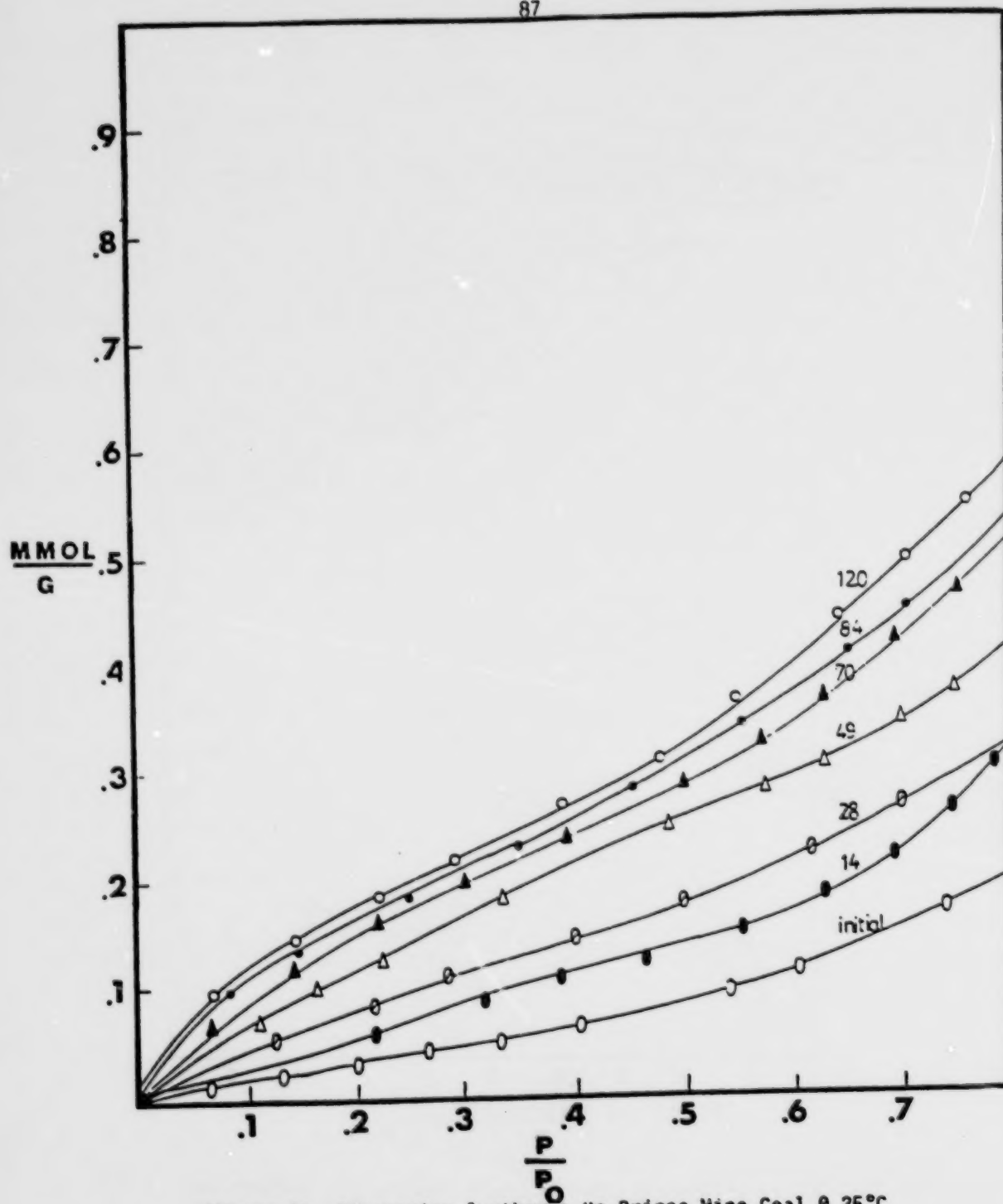


Figure 51 Adsorption Isotherms On Prince Mine Coal @ 25°C

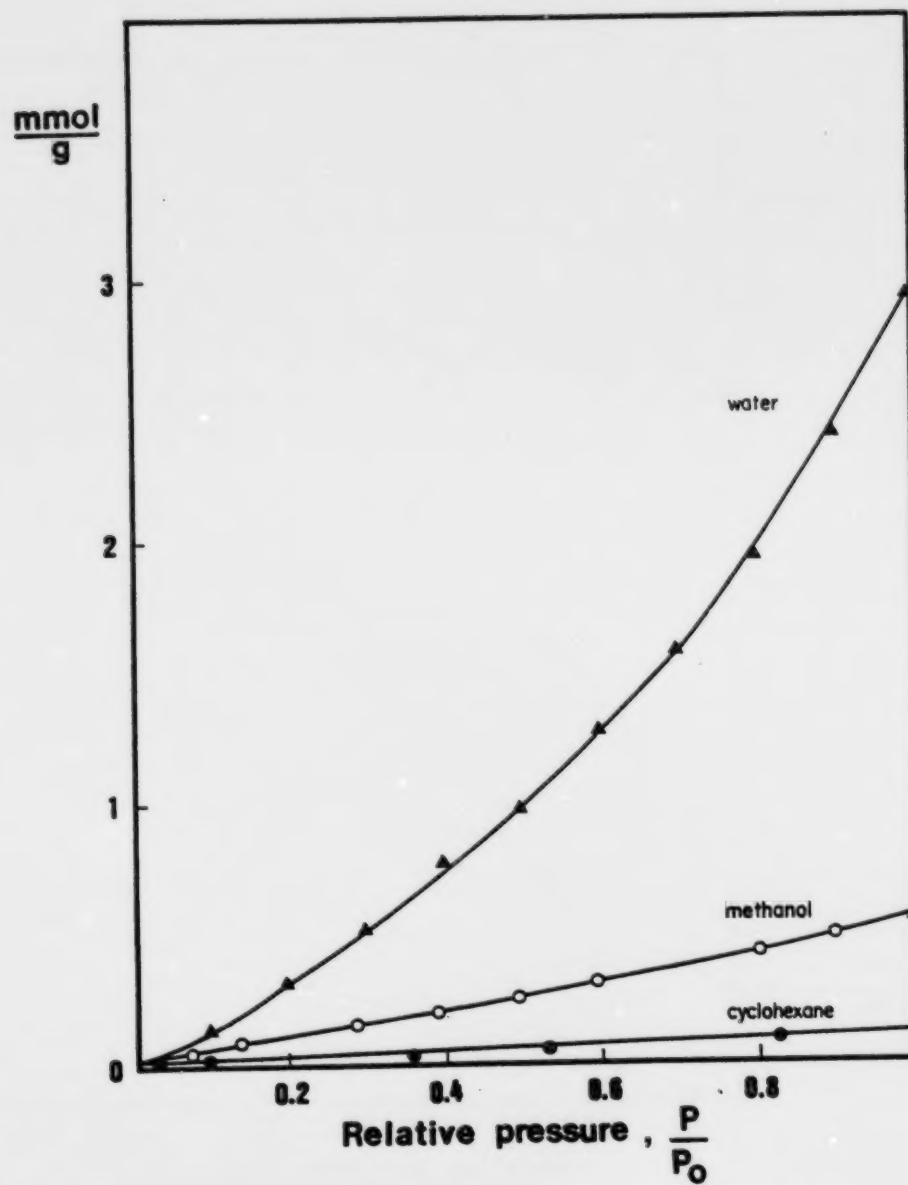


Figure 52 Adsorption Isotherm On Devco Metallurgical (No. 26) Coal @ 25°C

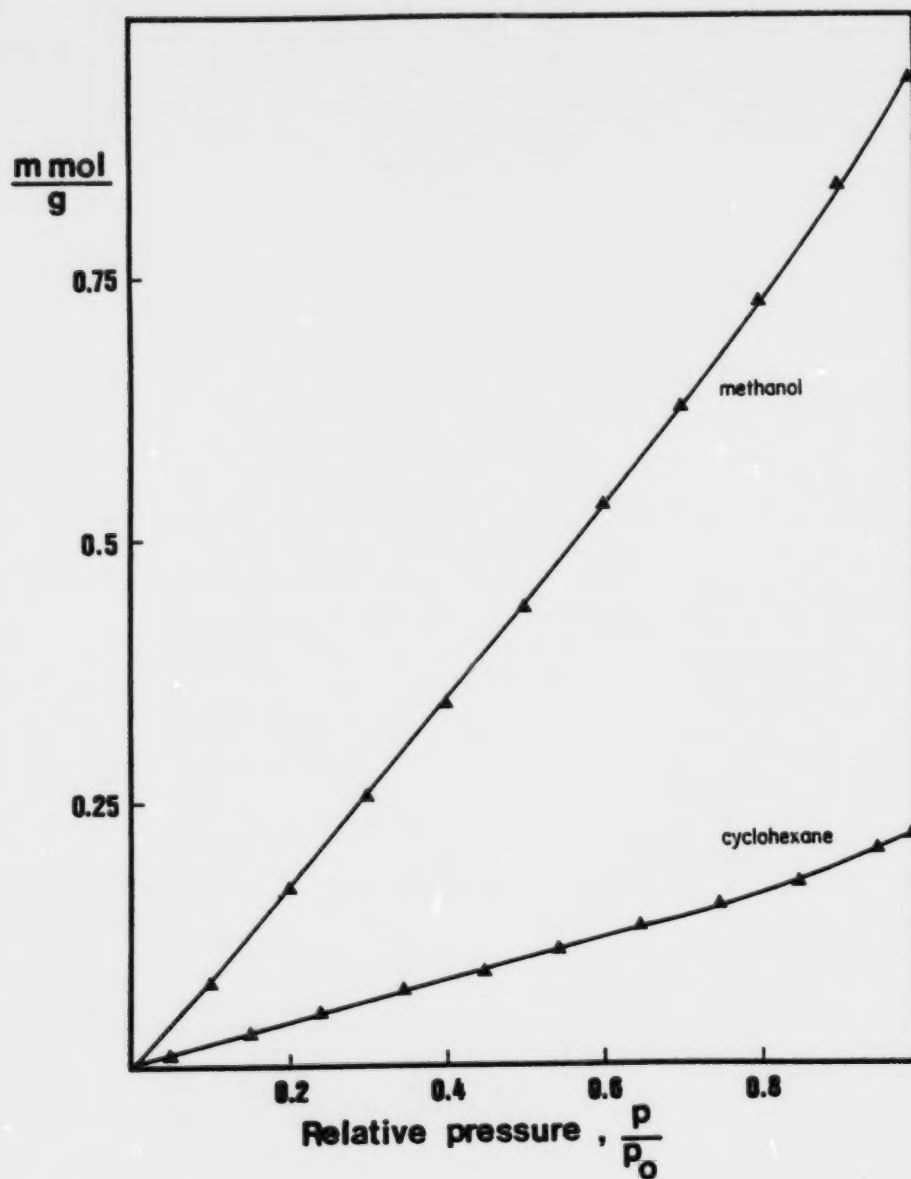


Figure 53 Adsorption Isotherms On Westville Coal @ 25°C

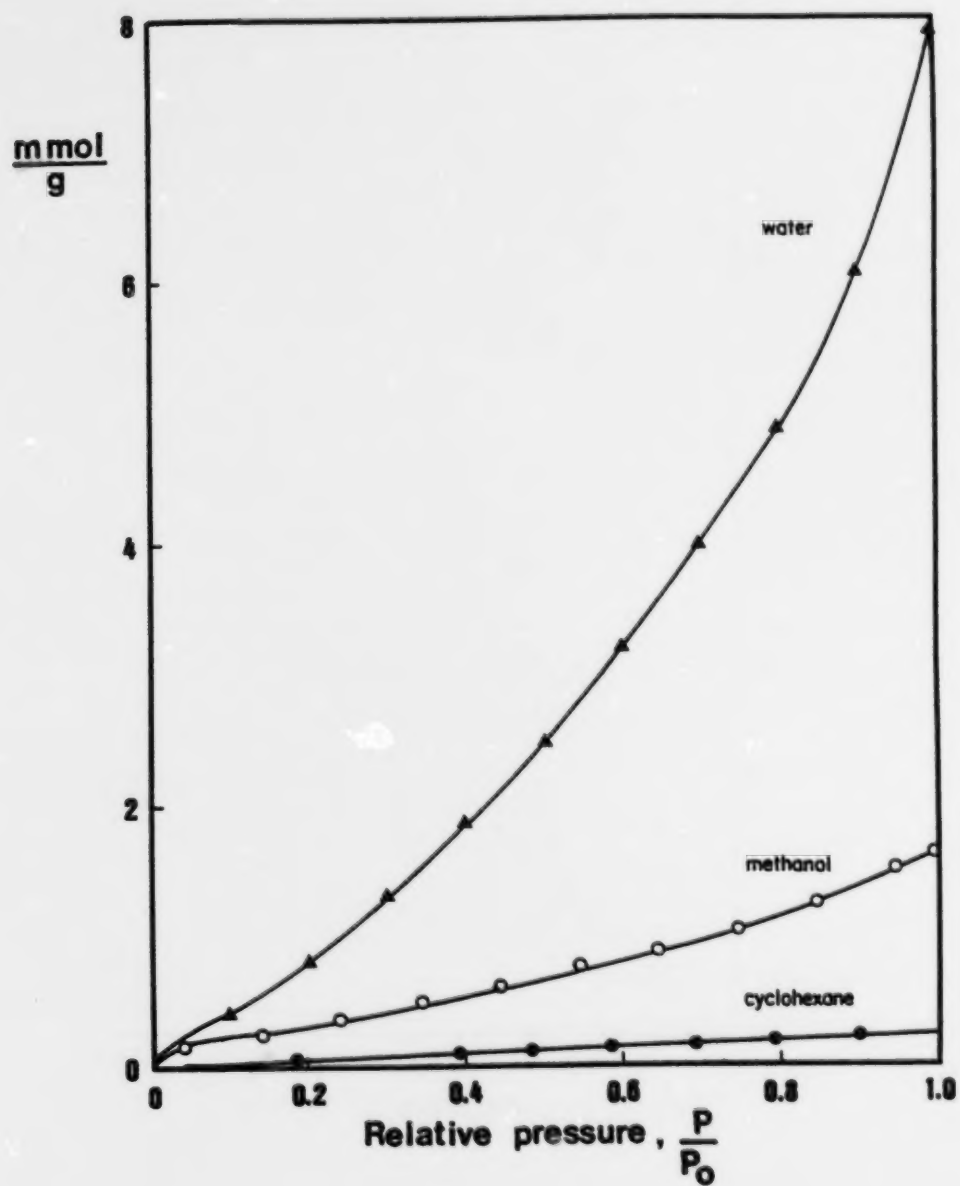


Figure 54 Adsorption Isotherms On Evans Coal @ 25°C

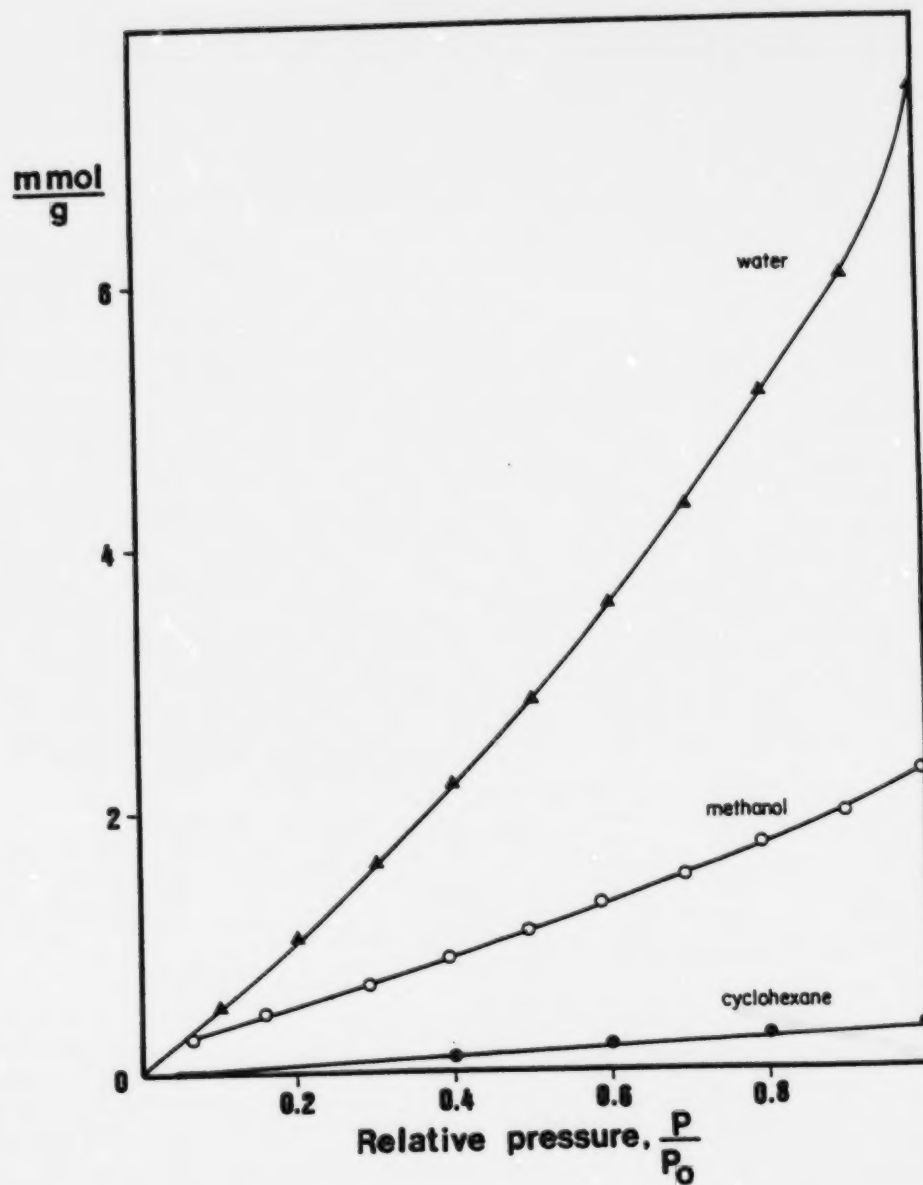


Figure 55 Adsorption Isotherms For Prince Mine Coal @ 25°C

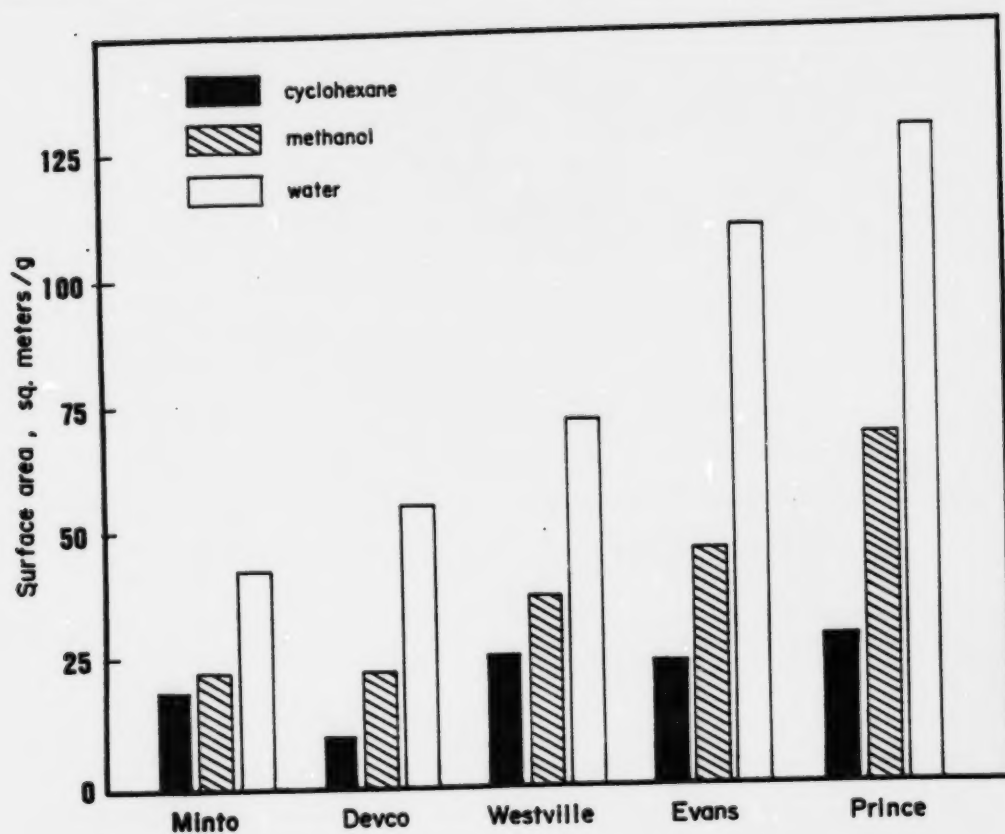


Figure 56 Comparison of the Surface Area, Evaluated @ 25°C Using Different Adsorbates of Different Maritime Coals

TABLE 23 The Surface Areas Obtained From Water,
Methanol and Benzene Adsorption

Time of Oxidation hrs)	Prince Mine (1139)			DEVCO No. 26 (1069)		
	S_{H_2O}	S_{MeOH}	$S_{C_6H_6}$	S_{H_2O}	S_{MeOH}	$S_{C_6H_6}$
0	5.5	19.0	20.2	6.2	21.4	23.6
14	8.7	18.1	20.4	9.1	20.0	23.9
28	11.4	16.2	17.7	10.7	19.1	18.2
49	16.7	14.1	14.8	15.8	17.6	16.1
70	20.9	15.0	14.2	19.1	17.2	15.9
84	22.0	16.0	16.0	20.0	17.1	16.2
120	23.1	18.3	18.3	20.7	19.1	19.0

*Surface area from isotherms at 25°C, $S(m^2/g)$

TABLE 24 Surface Characteristics of Maritime Coals

Coal	No. of Active Sites			
	n-Heptane $\times 10^{19}$	c-Hexane $\times 10^{19}$	Methanol $\times 10^{19}$	Water $\times 10^{21}$
Prince (PRO01)	3.81	8.18	37.02	1.19
Evans	2.59	6.28	24.64	1.06
Westville	2.69	7.11	20.60	0.66
Minto	1.72	5.19	11.10	0.39
Devco Met (1255)	2.73	2.75	12.65	0.52

TABLE 25 Effect of Coal Oxidation On the Number of Active Sites

Sample	N_{CH_3OH} $\times 10^{19}$	$N_{C_6H_6}$ $\times 10^{19}$	N_{H_2O} $\times 10^{19}$	$\frac{N_{CH_3OH}}{N_{C_6H_6}}$	$\frac{N_{H_2O}}{N_{C_6H_6}}$
Prince (1139)					
Initial	10.49	3.88	5.19	2.70	1.34
14 hrs	10.00	3.92	8.21	2.55	2.09
28 "	9.72	3.40	10.75	2.85	3.16
49 "	7.79	2.85	15.75	2.73	5.53
70 "	8.28	2.73	19.71	3.03	7.22
84 "	8.84	3.08	20.75	2.87	6.73
120 "	10.11	3.52	21.80	2.87	6.20
Devco No. 26 (1069)					
Initial	11.82	4.53	5.84	2.61	1.29
14 hrs	11.05	4.60	8.58	2.40	1.87
28 "	10.55	3.50	10.10	3.01	2.89
49 "	9.72	3.10	14.91	3.13	4.81
70 "	9.50	3.06	18.02	3.10	5.89
84 "	9.44	3.11	18.86	3.03	6.05
120 "	10.55	3.65	19.52	2.90	5.35

Proper interpretation of the above data is complicated by the varying accessibility of different sorbates and by the tendency of water to be adsorbed on the organic active sites as well as on the inorganic active sites present in the ash constituents (Kaolinite, Montmorillonite, $FeSO_4$) etc). It is, however, clearly evident that the number of hydrophillic active sites progressively increase with increasing extent of oxidation (Table 25).

The strong dependence on the specific interaction between the adsorbate and the progressively heterogeneous coal surface is quite evident from the data obtained. Thus, as can be seen from Figure 57, the affinity of coal surfaces to water was found to increase with the extent of surface oxidation;

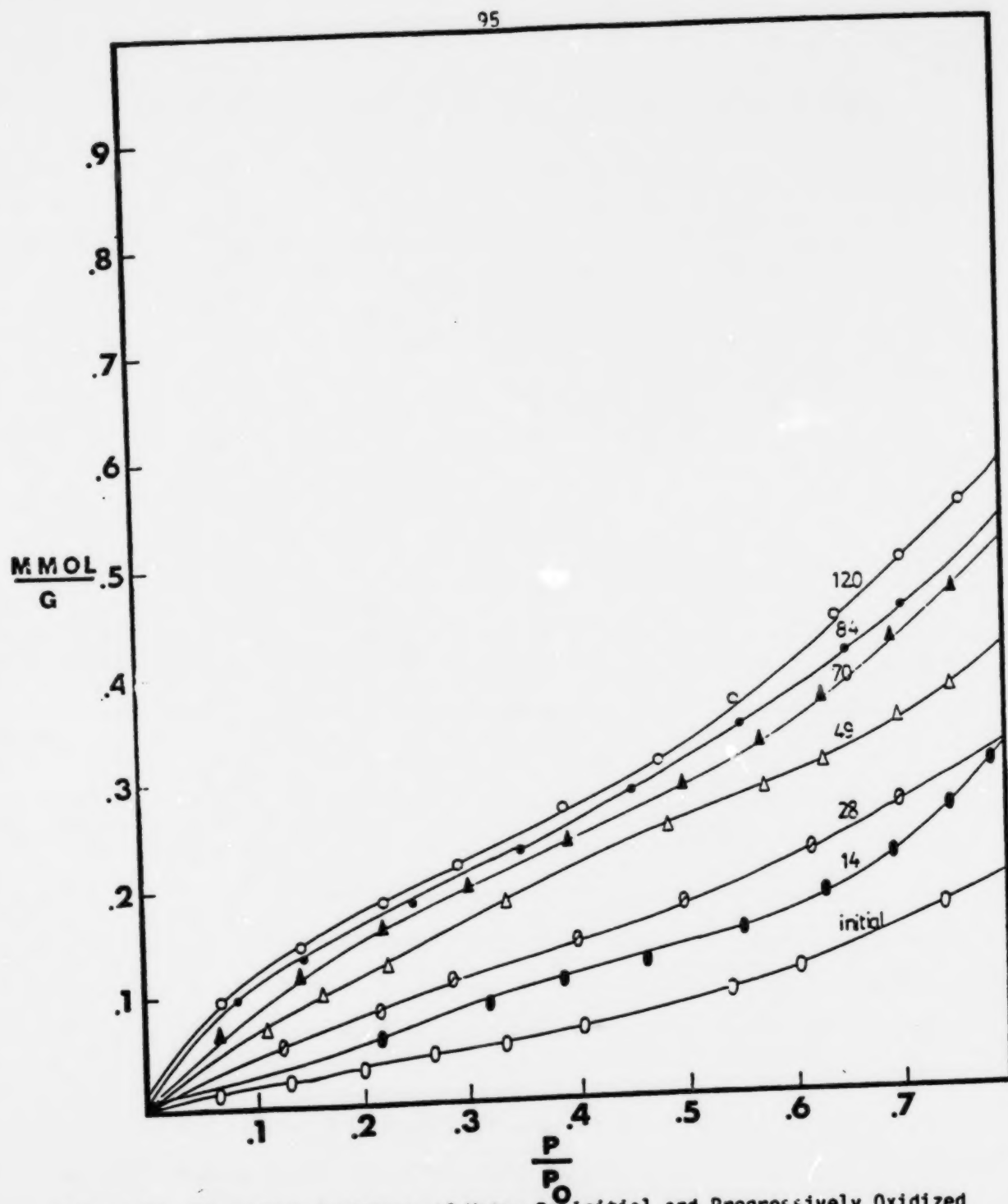


Figure 57 Adsorption Isotherms of Water On Initial and Progressively Oxidized Prince Mine Coals (-200 +270 Mesh, 25°C)

suggesting a greater tendency for water retention as a result of the formation of polar oxygen-containing functional groups on the surface of the coal. On the other hand, the affinity of coal surfaces towards methanol was found to increase as the coal surface is slightly oxidized (Figure 58), reaching a peak after 28 hours of oxidation. Further oxidation of the coal results in reducing its affinity to adsorb methanol, ultimately reaching values lower than the initial coal samples after 120 hours.

Adsorption of benzene on the surface of the coal similarly exhibits a minimum (occurring at 48 hours for the Prince Mine and 70 hours for the No. 26 metallurgical coals) beyond which the surface affinity for benzene increases.

The isotherms were also used to evaluate the pore structure of the various coals tested and the resulting values (Figures 59 and 60) suggest significant variation between the various Maritime coals. This in turn, could possibly explain the variation in their reactivity and response to surface-controlled beneficiation processes. The effect of coal oxidation on the main pore structure parameters is shown in Table 26.

III.7.2 Reproducibility of Isotherms

The reproducibility of this technique was evaluated based on the significant parameters (such as surface area and total pore volume) derived from the isotherm. The data obtained (Table 27) clearly indicate the high reproducibility achievable using this technique.

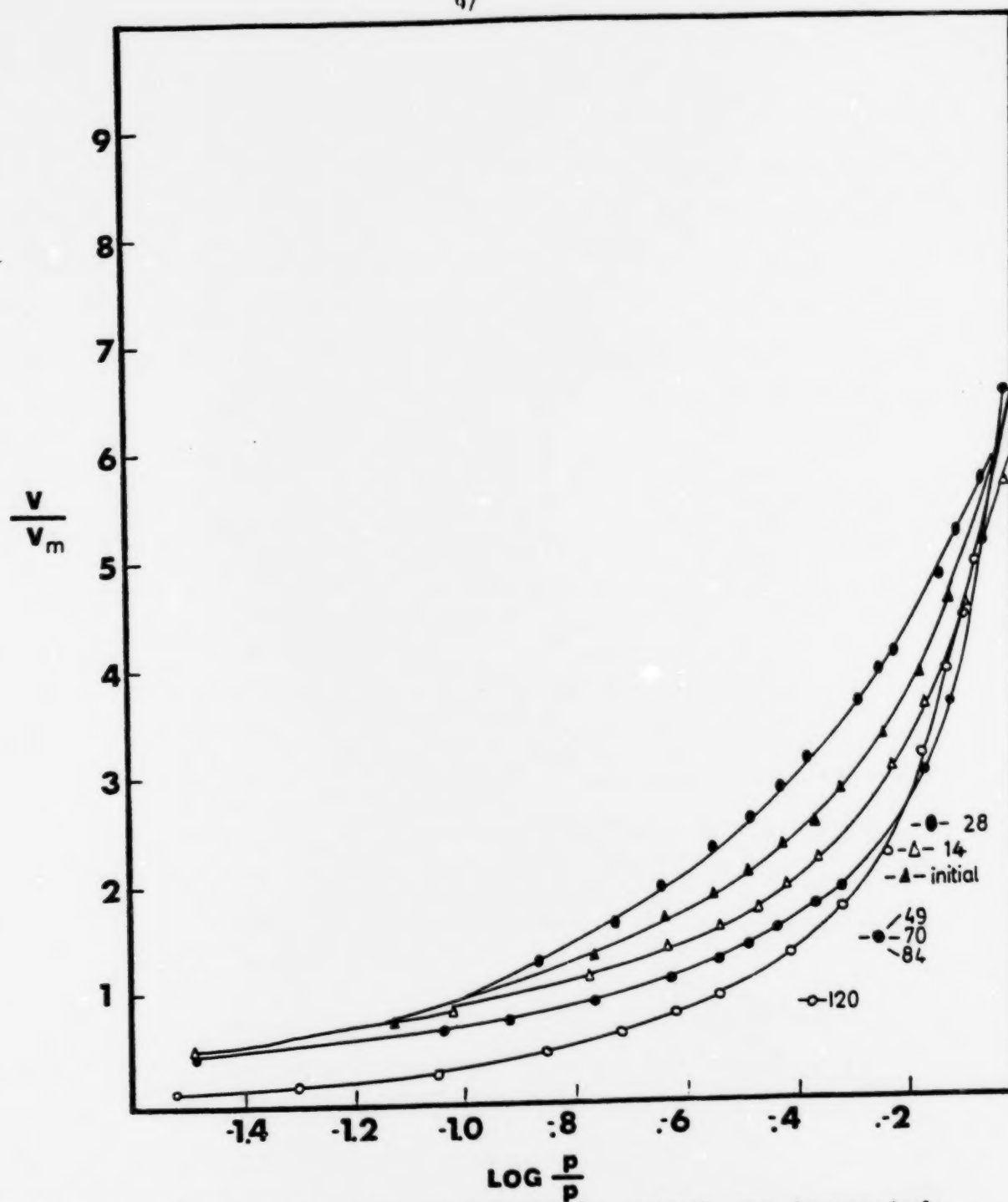


Figure 58 Adsorption Isotherms of Methanol On Initial and Progressively Oxidized Prince Mine Coals (-200 +270 Mesh, 25°C)

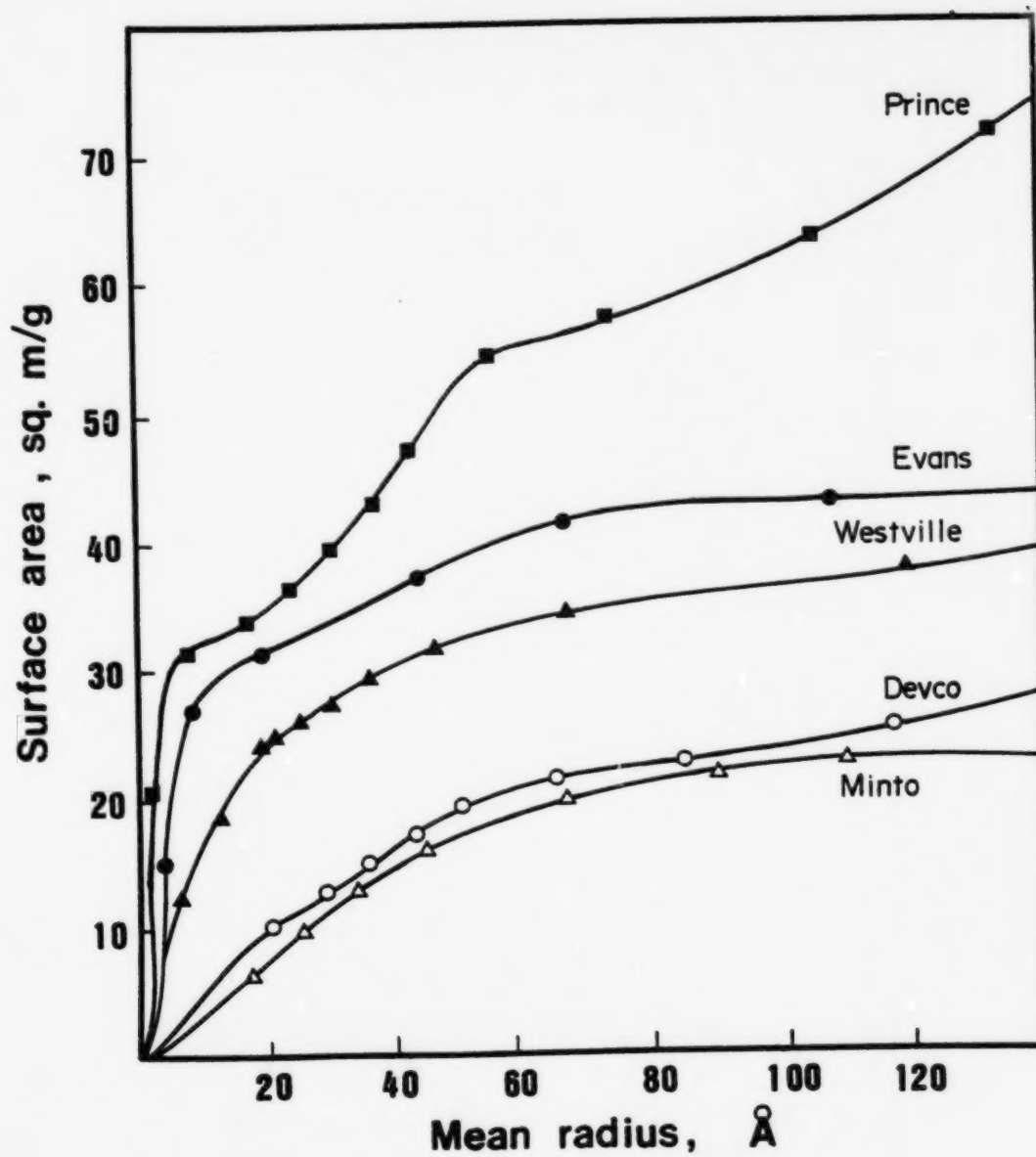


Figure 59 Cumulative Pore Size Distributions For Coal Investigated (Methanol @ 25°C)

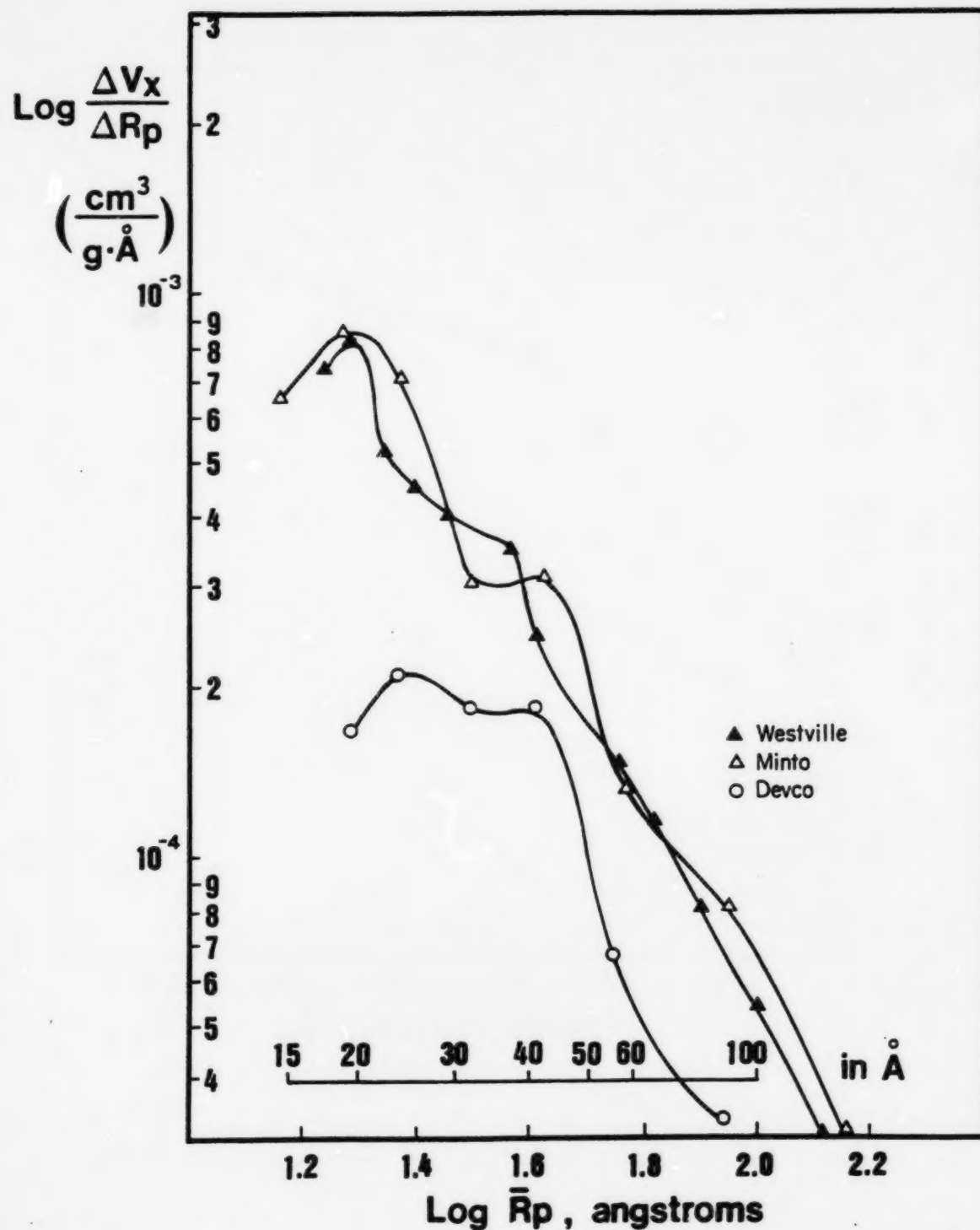


Figure 60 Pore Size Distribution For Selected Maritime Coals (Methanol @ 25°C)

TABLE 26 Main Pore Structure Parameters (Benzene @ 25°C)

Sample	Total surface area m^2/g	Transitional S.A. m^2/g	Micropore S.A. m^2/g	Total volume cm^3/g	Transitional volume	Micropore volume cm^3/g
Prince Mine						
Oxidized 14 hrs.	20.2	14.9	5.3	0.0421	0.0224	0.0040
Oxidized 28 hrs.	20.4	15.4	5.0	0.0427	0.0230	0.0038
Oxidized 49 hrs.	17.7	12.1	5.6	0.0354	0.0181	0.0042
Oxidized 70 hrs.	14.8	12.0	2.8	0.0340	0.0180	0.0021
Oxidized 84 hrs.	16.0	12.1	3.9	0.0335	0.0180	0.0029
Oxidized 120 hrs.	15.6	11.9	3.7	0.0340	0.0179	0.0028
	18.3	12.8	5.5	0.0361	0.0194	0.0041
Devco MET						
Oxidized 14 hrs.	23.6	17.6	6.0	0.0491	0.0243	0.0048
Oxidized 28 hrs.	23.9	18.1	5.8	0.0500	0.0249	0.0046
Oxidized 49 hrs.	18.2	14.0	4.2	0.0380	0.0195	0.0034
Oxidized 70 hrs.	16.1	12.2	3.9	0.0374	0.0190	0.0031
Oxidized 84 hrs.	15.9	12.1	3.8	0.0368	0.0191	0.0030
Oxidized 120 hrs.	16.2	12.0	4.2	0.0365	0.0186	0.0034
	19.0	13.6	5.4	0.0400	0.0210	0.0043

**TABLE 27 Effect of Coal Oxidation On the Reproducibility of
Vapor Isotherm Measurements**

Oxidation Time	No. of Replicates	Error In Surface Area Measurement ($5n-1/X$) % age		
		Water	Methanol	Benzene
0	3	4.1	0.6	4.2
14	3	4.3	0.6	3.8
28	3	5.0	0.8	3.7
49	3	4.2	3.6	4.3
70	3	5.1	6.3	5.1
84	3	5.7	6.0	5.0
120	3	4.8	4.2	6.2

III.7.3 Application To Western Coal Samples

The adsorption characteristics of six Western coal samples were evaluated using three different adsorbates, namely n-Heptane, Methanol and water vapours. The results obtained are shown in Figures 61 to 66, which are based on tests conducted in triplicate with a variance smaller than $\pm 5\%$. The data clearly indicate that all the coal tested have the greatest affinity to water, followed by Methanol and ultimately to n-Heptane. A comparative evaluation of the variation of these affinities amongst different coal samples is shown by their respective BET surface area values (Figures 67 to 70).

The coals' affinity to water and methanol was found to increase with increasing hydrophilicity, while conversely, its affinity to n-Heptane is reduced. The corresponding number of active sites are, therefore, listed in Table 28 and are used to calculate two ratios of the hydrophilic to

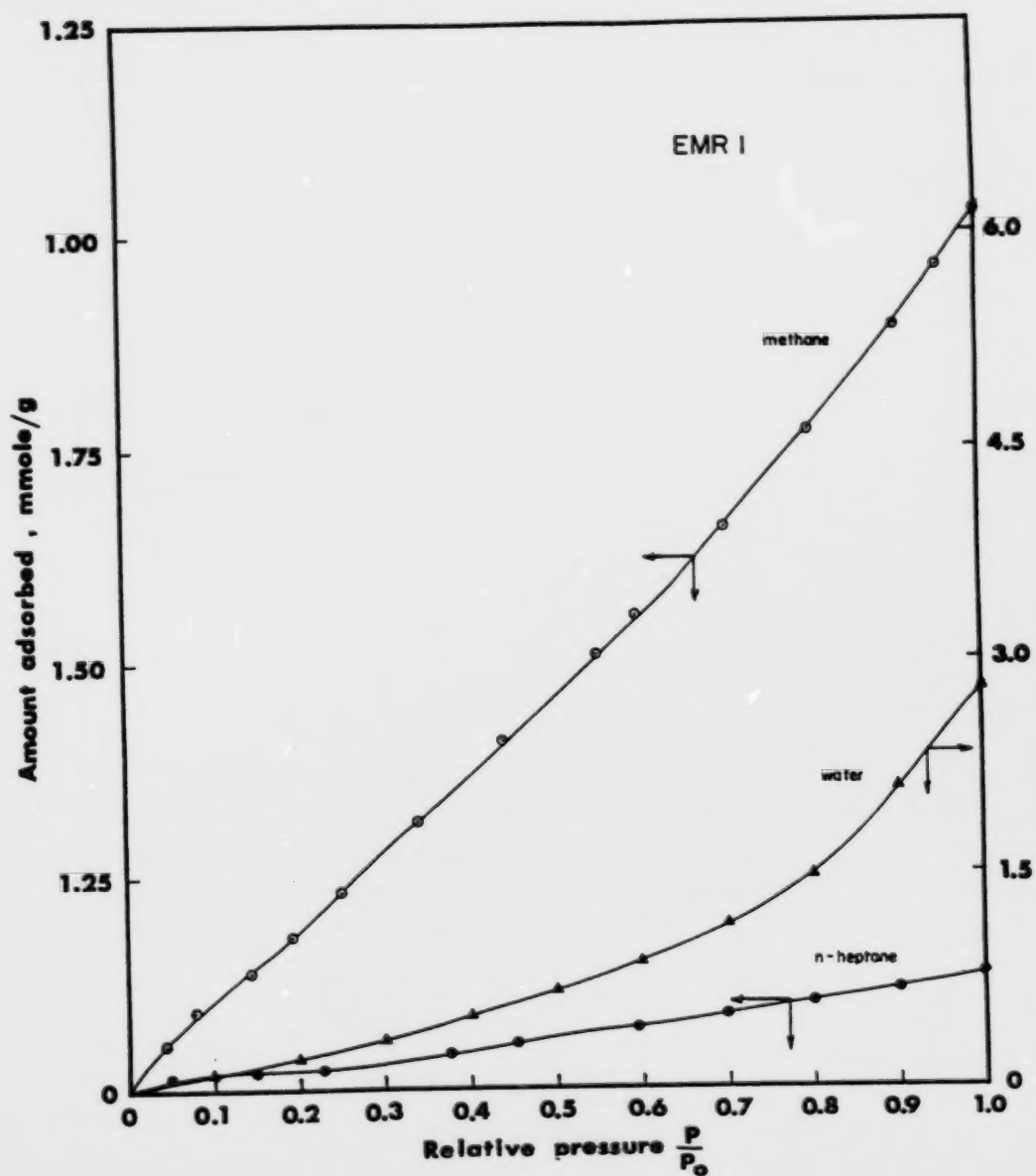


Figure 61 Adsorption Isotherms For EMR Sample No. 1 @ 25°C

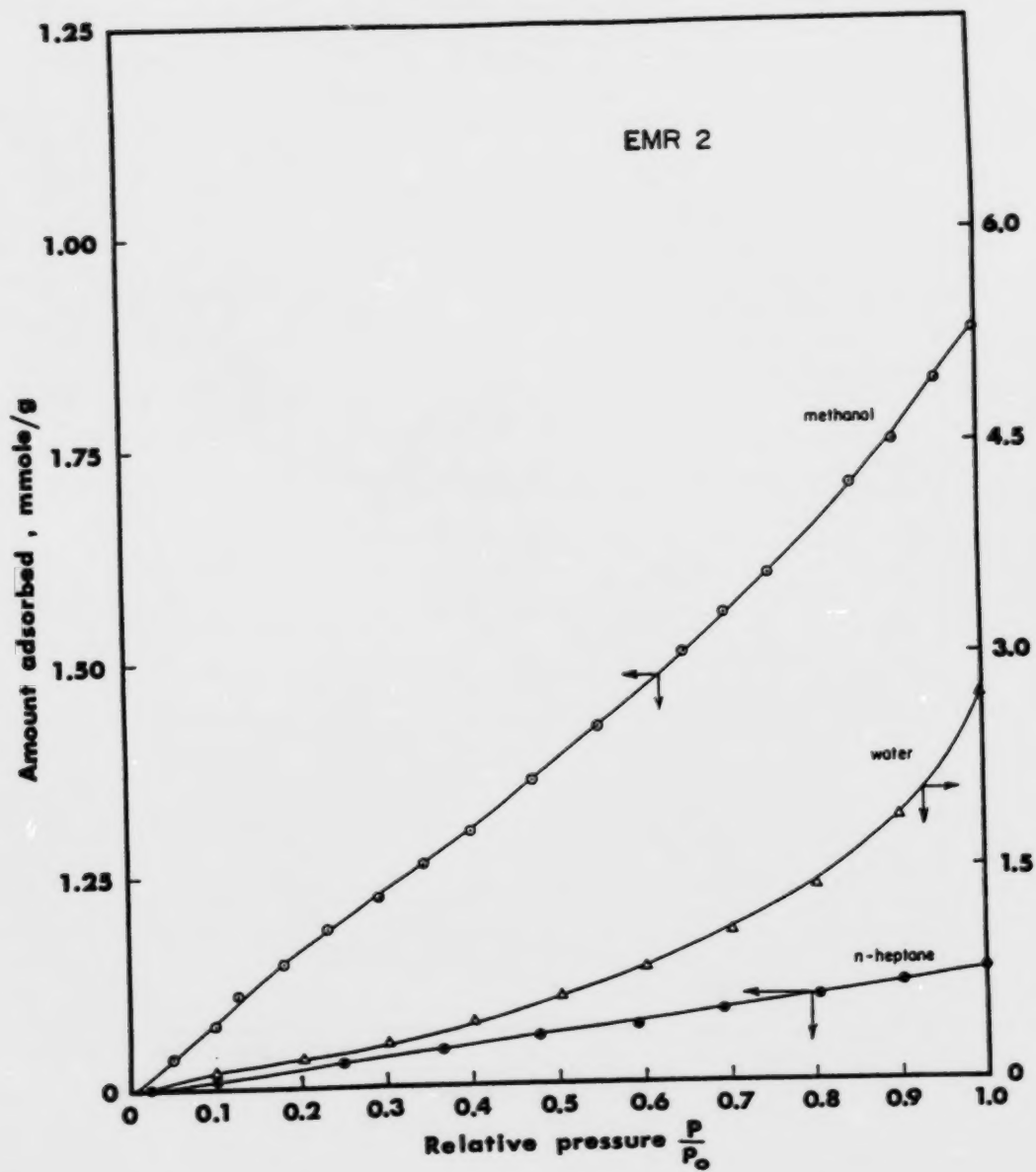


Figure 62 Adsorption Isotherms For EMR Sample No. 2 @ 25°C

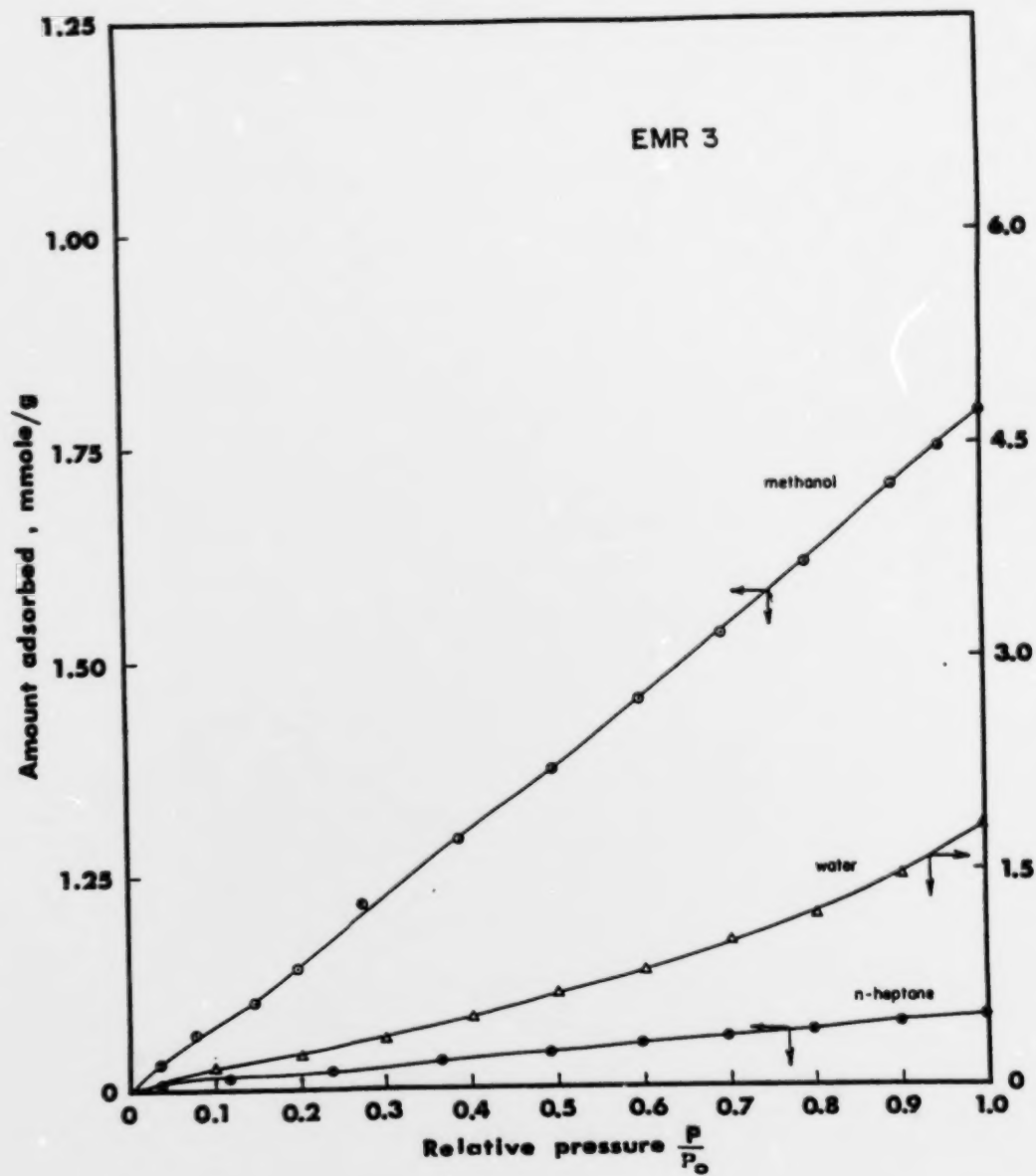


Figure 63 Adsorption Isotherms For EMR Sample No. 3 @ 25°C

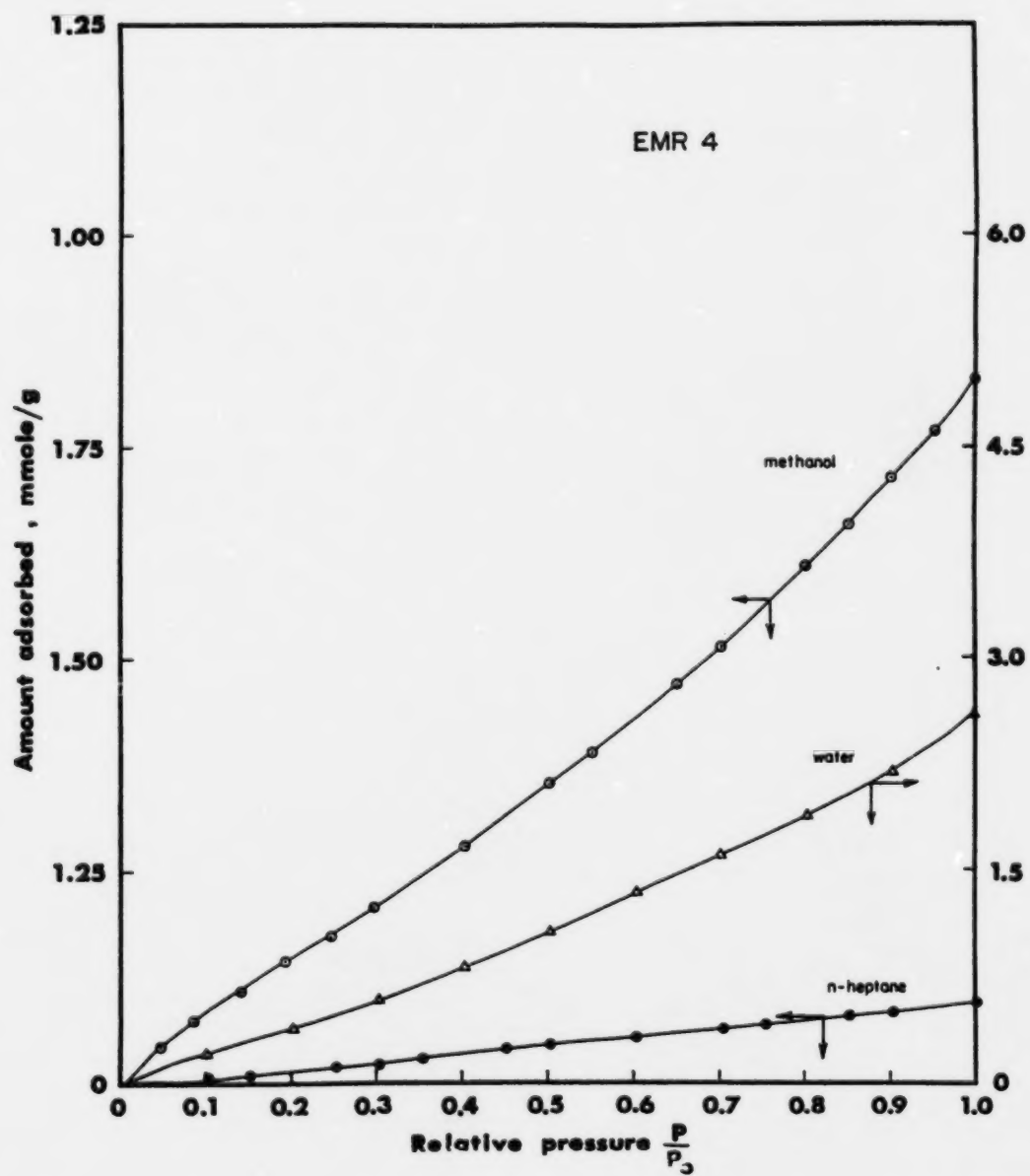


Figure 64 Adsorption Isotherms For EMR Sample No. 4 @ 25°C

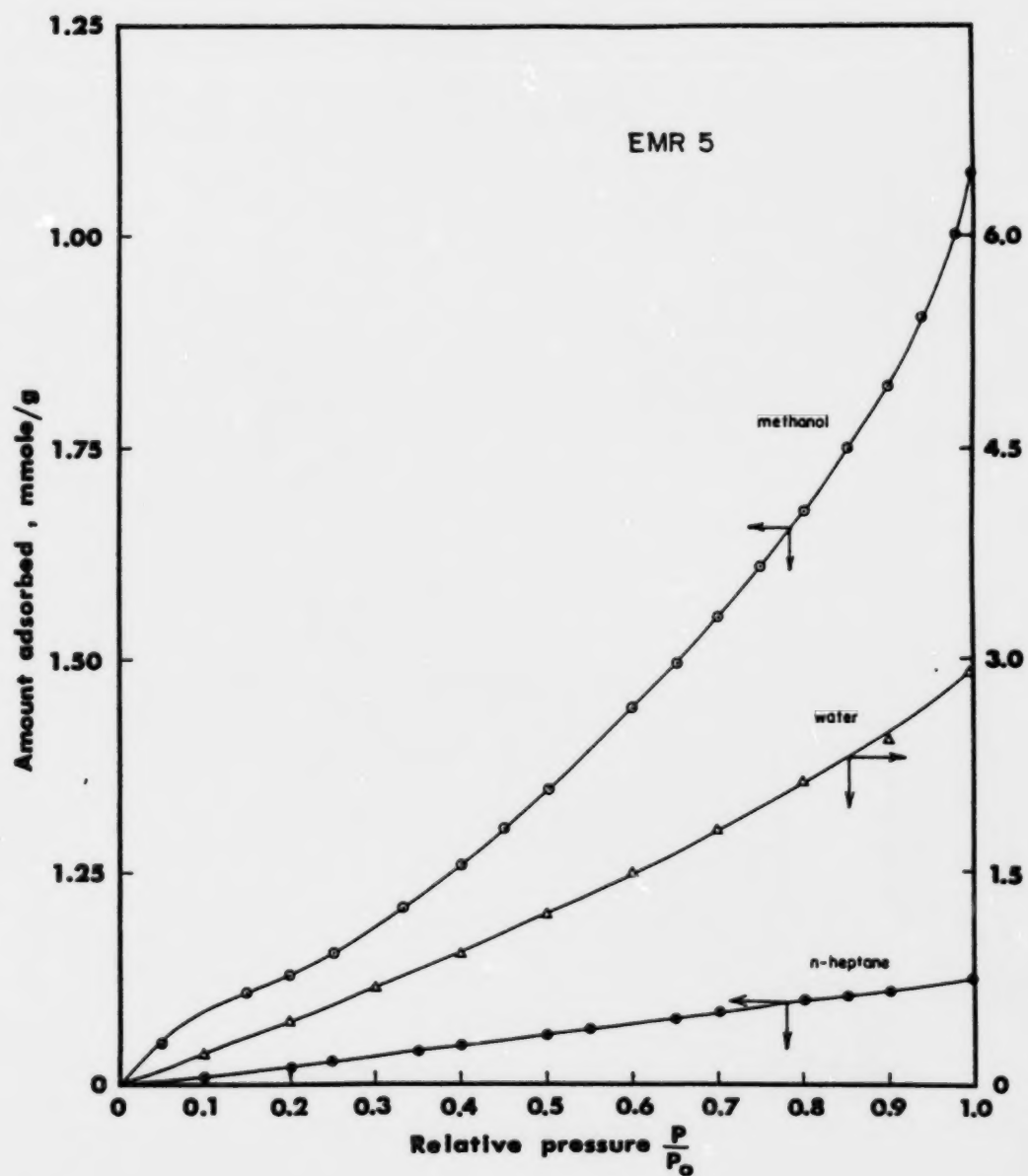


Figure 65 Adsorption Isotherms For EMR Sample No. 5 @ 25°C

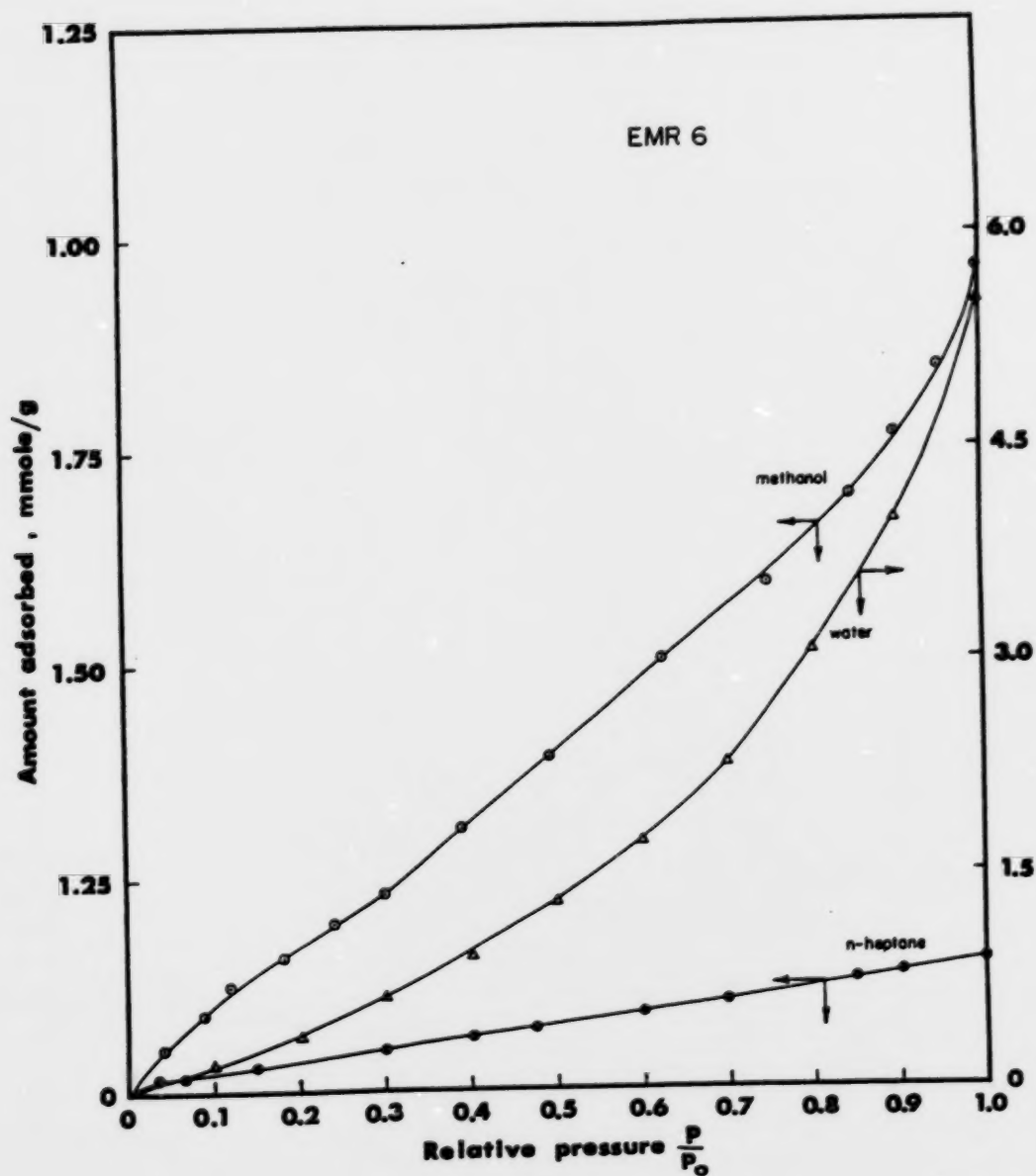


Figure 66 Adsorption Isotherms For EMR Sample No. 6 @ 25°C

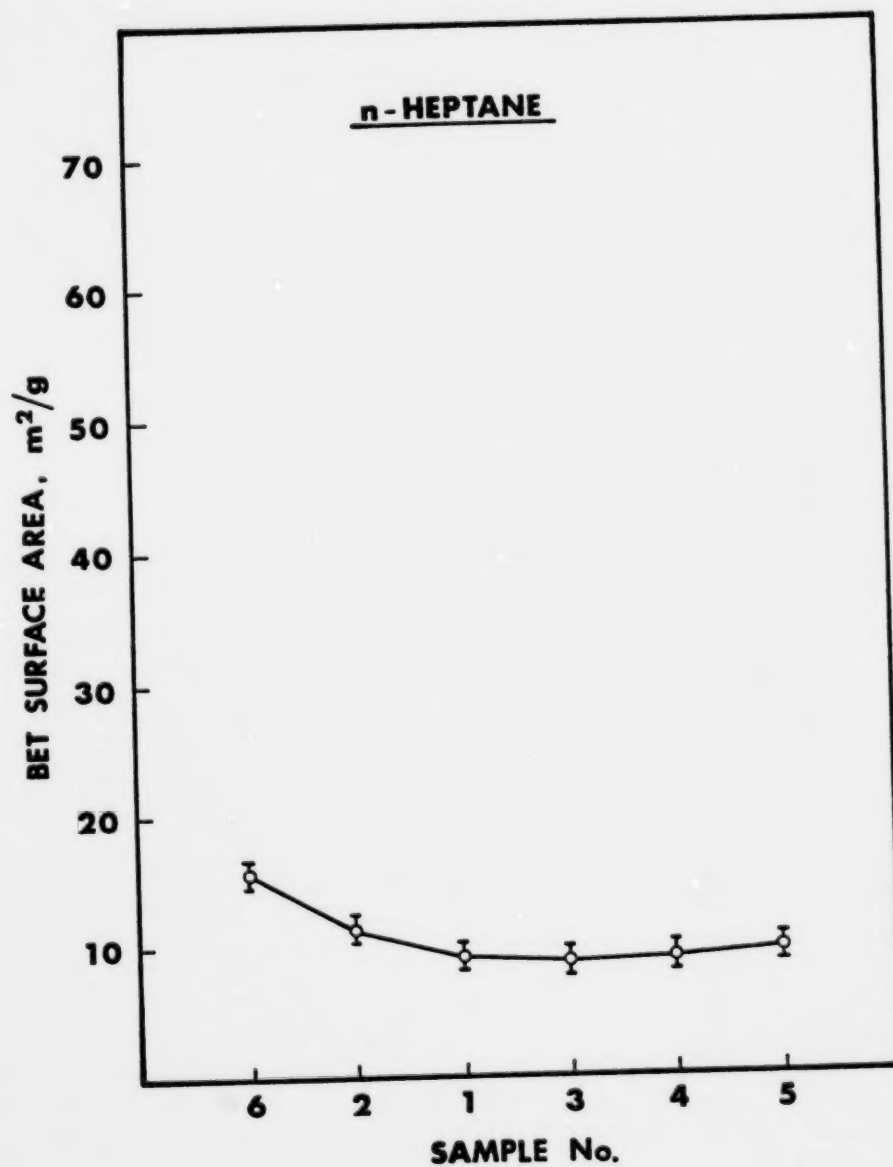


Figure 67 BET Surface Areas For Western Coal Samples (n-Heptane @ 25°C)

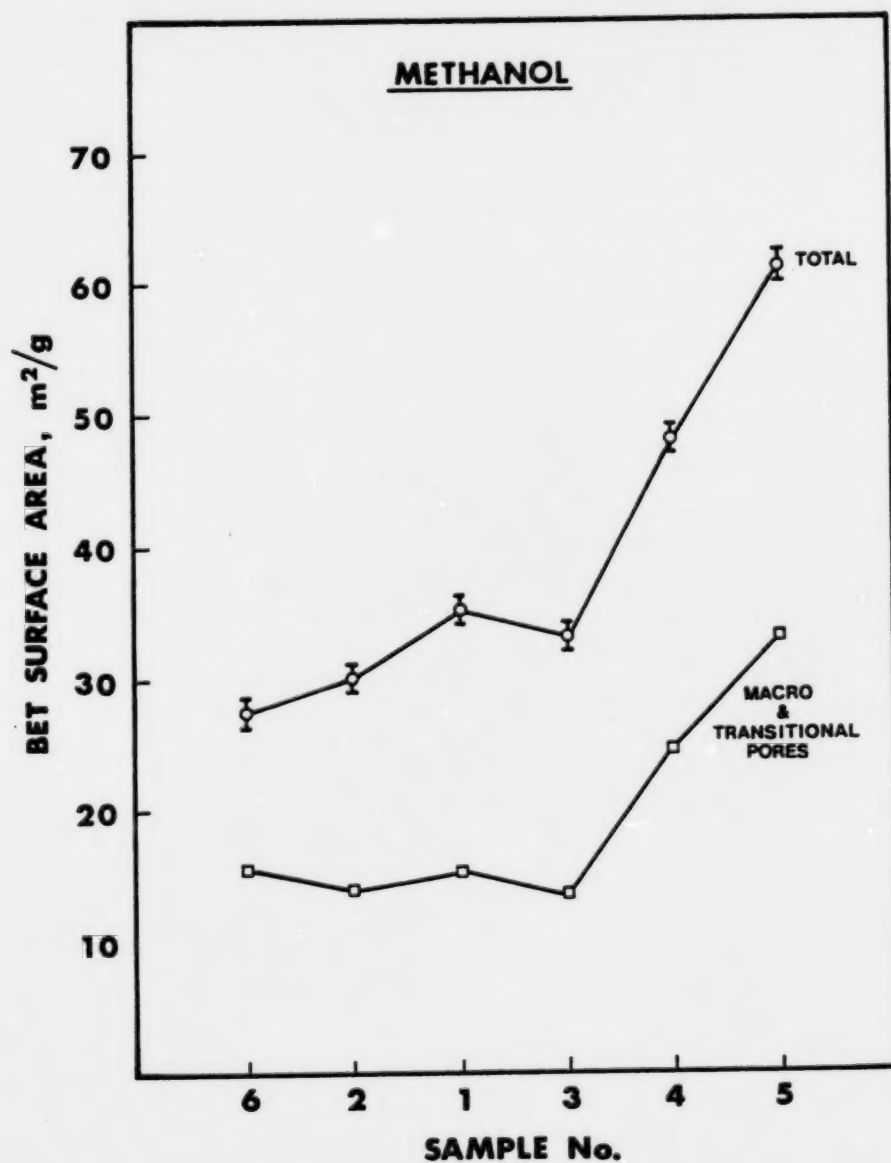


Figure 68 BET Surface Areas For Western Coal Samples (Methanol @ 25°C)

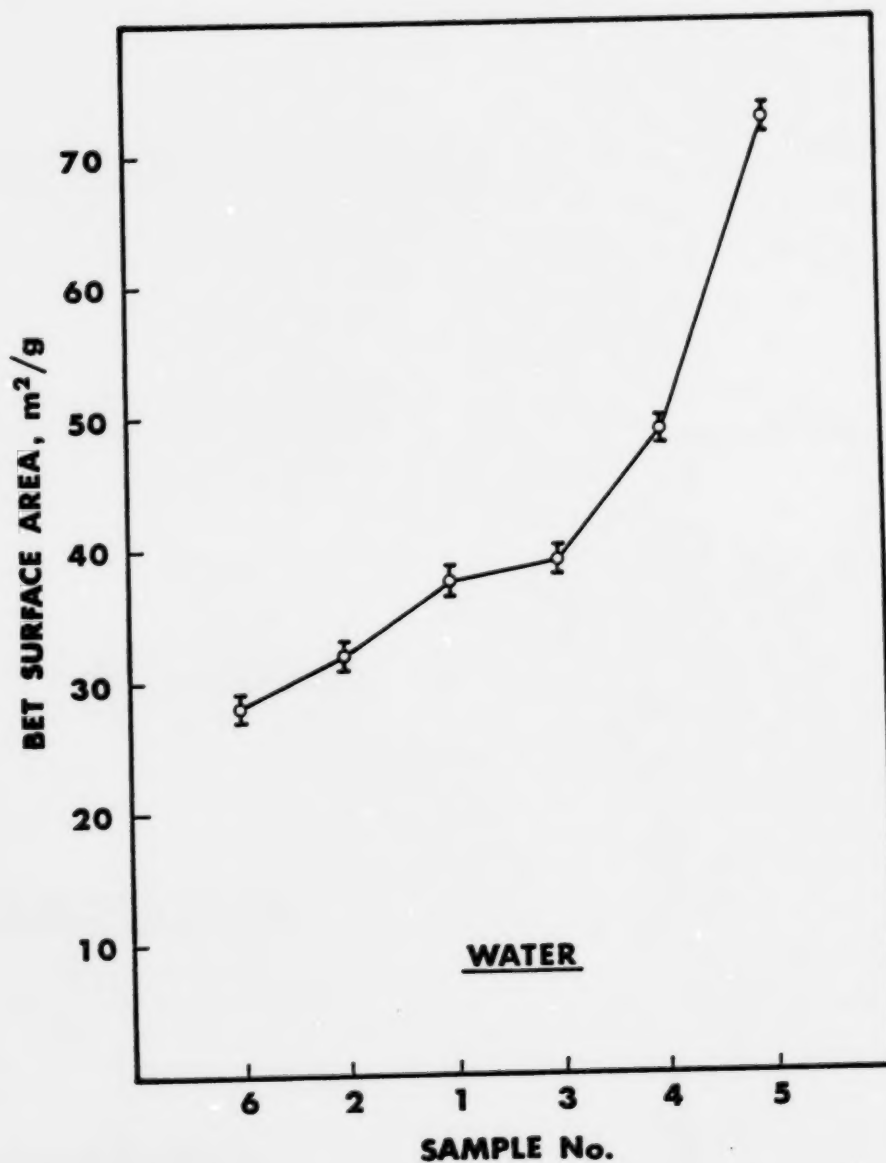


Figure 69 BET Surface Areas For Western Coal Samples (Water @ 25°C)



Figure 70 Comparison of the Surface Area (Evaluated @ 25°C Using Different Adsorbates) of Different Western Coals

hydrophobic active sites. The first one is based on water as indicator of the hydrophilic active sites, while the second uses Methanol. Their variation as a function of the coal's hydrophilicity is depicted in Figures 71 and 72.

TABLE 28 Number of Active Sites On the Western Coal Samples Investigated

Sample	$\frac{N_{H_2O}}{x \cdot 10^{19}}$	$\frac{N_{CH_3OH}}{x \cdot 10^{19}}$	$\frac{N_{C_7H_{16}}}{x \cdot 10^{19}}$	$\frac{N_{CH_3OH}}{N_{C_7H_{16}}}$	$\frac{N_{H_2O}}{N_{C_7H_{16}}}$
Prince (PR001)	119	37.02	3.81	9.72	31.23
Devco No. 26	52	12.65	2.73	4.63	19.05
EMR 1	5.87	3.24	0.26	12.11	21.9
EMR 2	5.02	2.74	0.31	8.59	15.76
EMR 3	6.12	3.06	0.25	11.79	23.56
EMR 4	7.64	4.41	0.25	17.37	30.09
EMR 5	11.27	5.56	0.27	20.12	40.75
EMR 6	43.86	2.49	0.43	5.70	10.22

The isotherms were also used to evaluate the pore structure of the Western coal samples and it is rather interesting to notice the significant difference resulting from the use of polar and nonpolar adsorbates (Figures 72 to 78). The pore size distribution (Figure 79) also shows significant variation amongst different coal samples. However, without access to the origin and history of the various Western coal samples it is rather difficult to discuss the significant variation in pore size distributions. The main pore-structure parameters for Western coals are listed in Table 29.

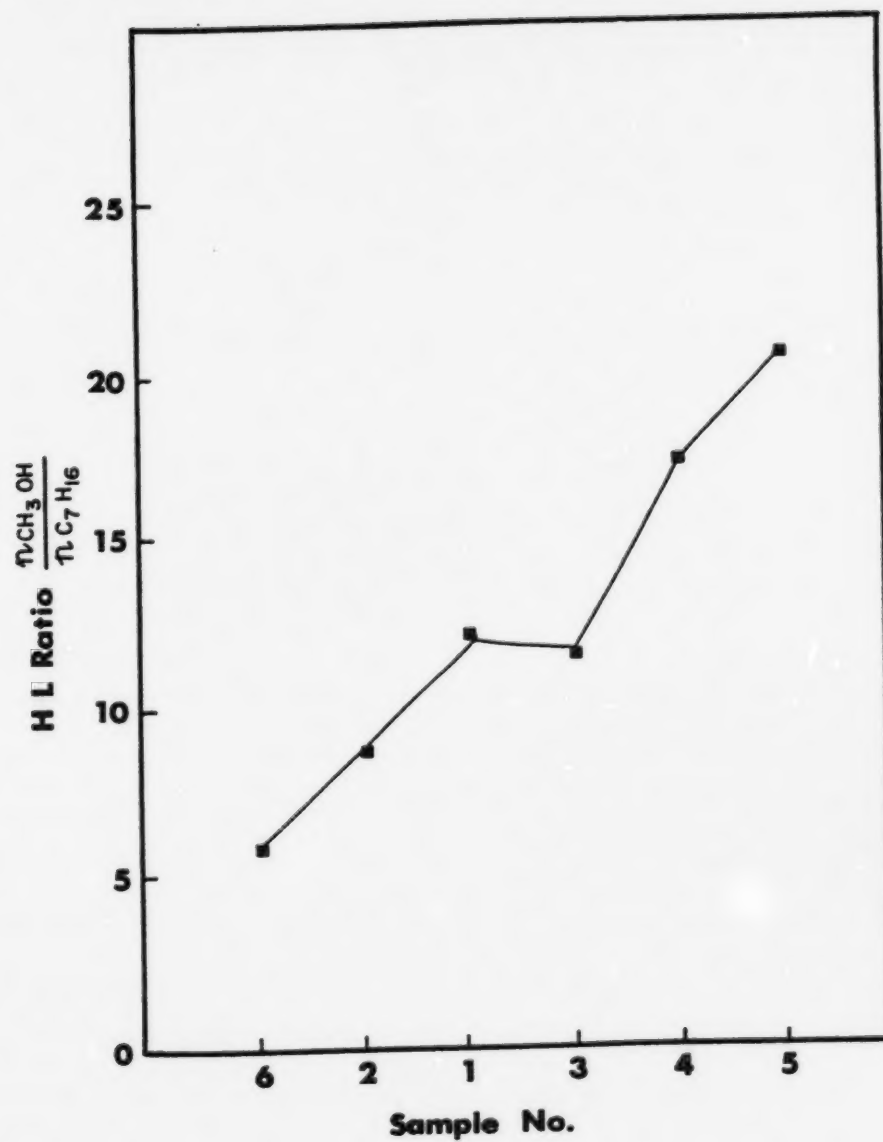


Figure 71 Variation of the Hydrophilic to Lyophilic Ratio of Active Sites Amongst the Coals Tested

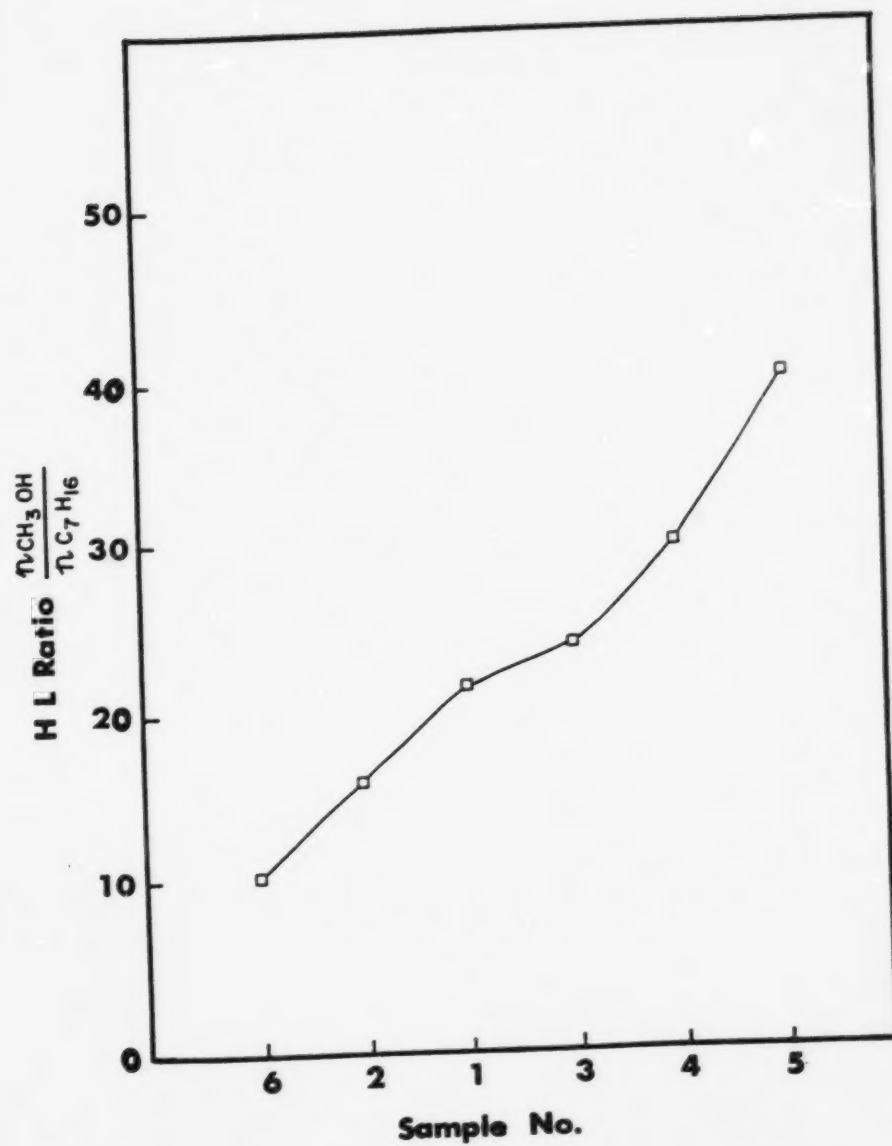


Figure 72 Variation of the Hydrophillic To Lyophillic Ratio of Active Sites Amongst the Western Coals Tested

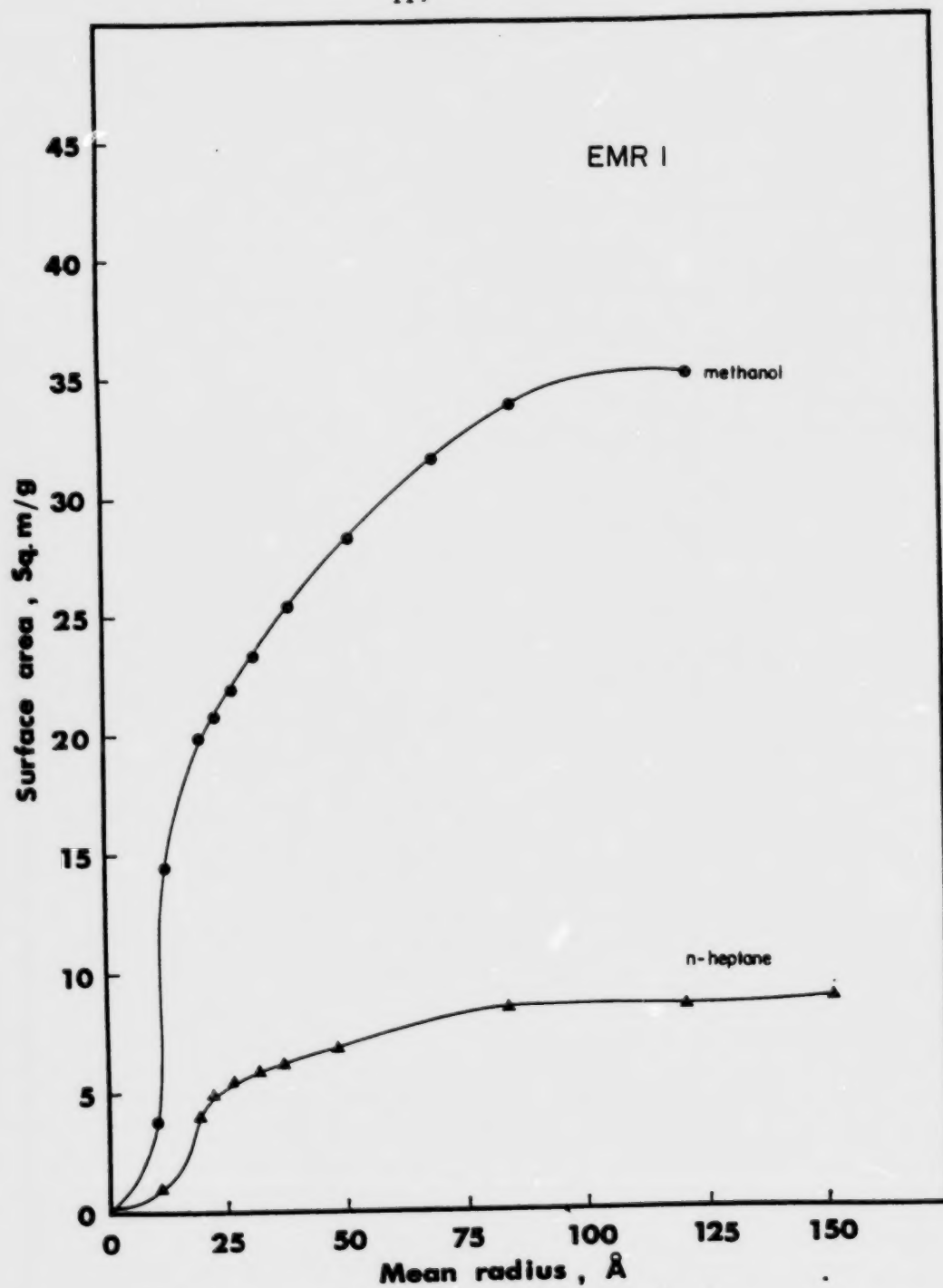


Figure 73 Pore Structure of EMR Sample No. 1

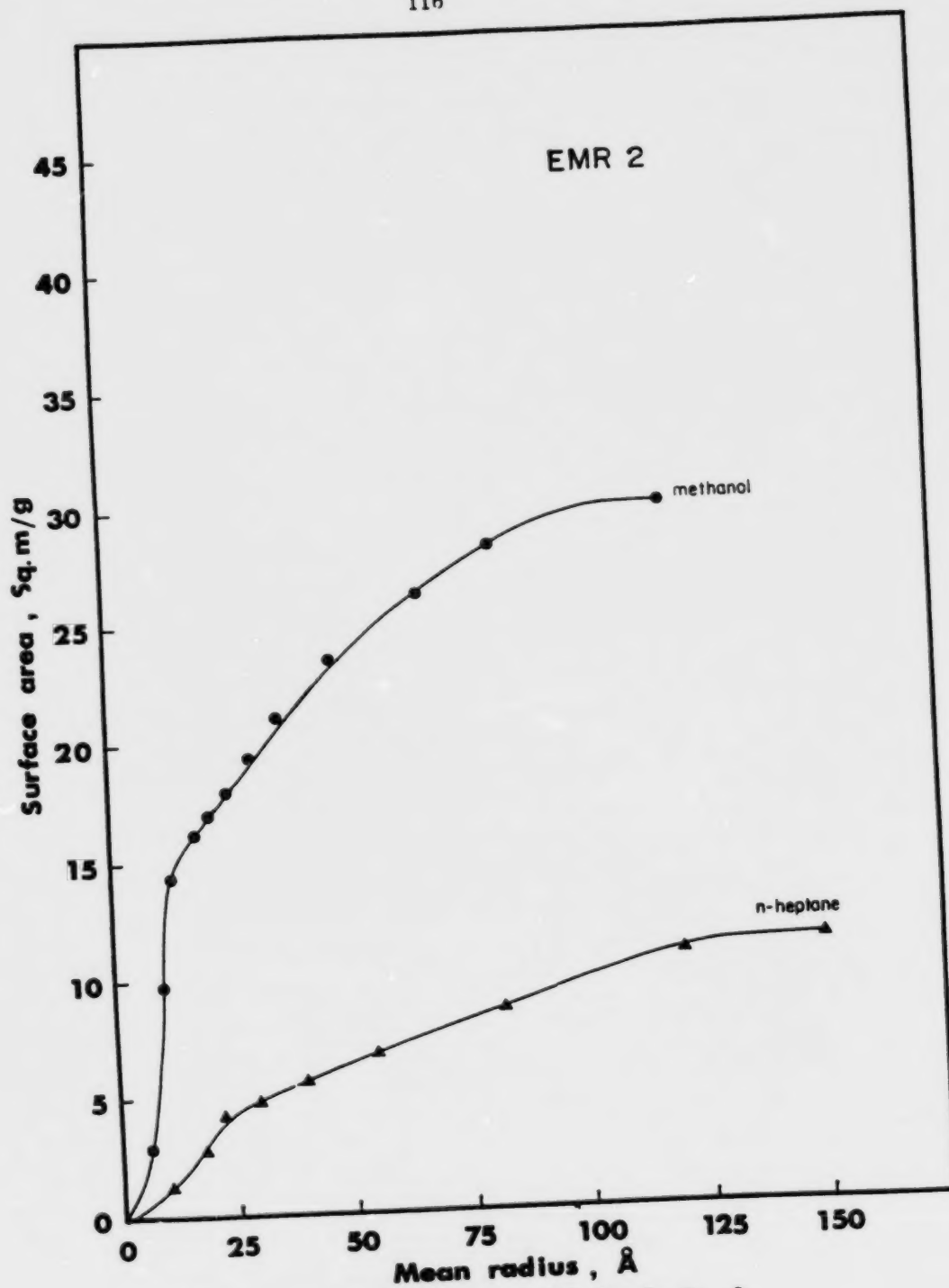


Figure 74 Pore Structure of EMR Sample No. 2

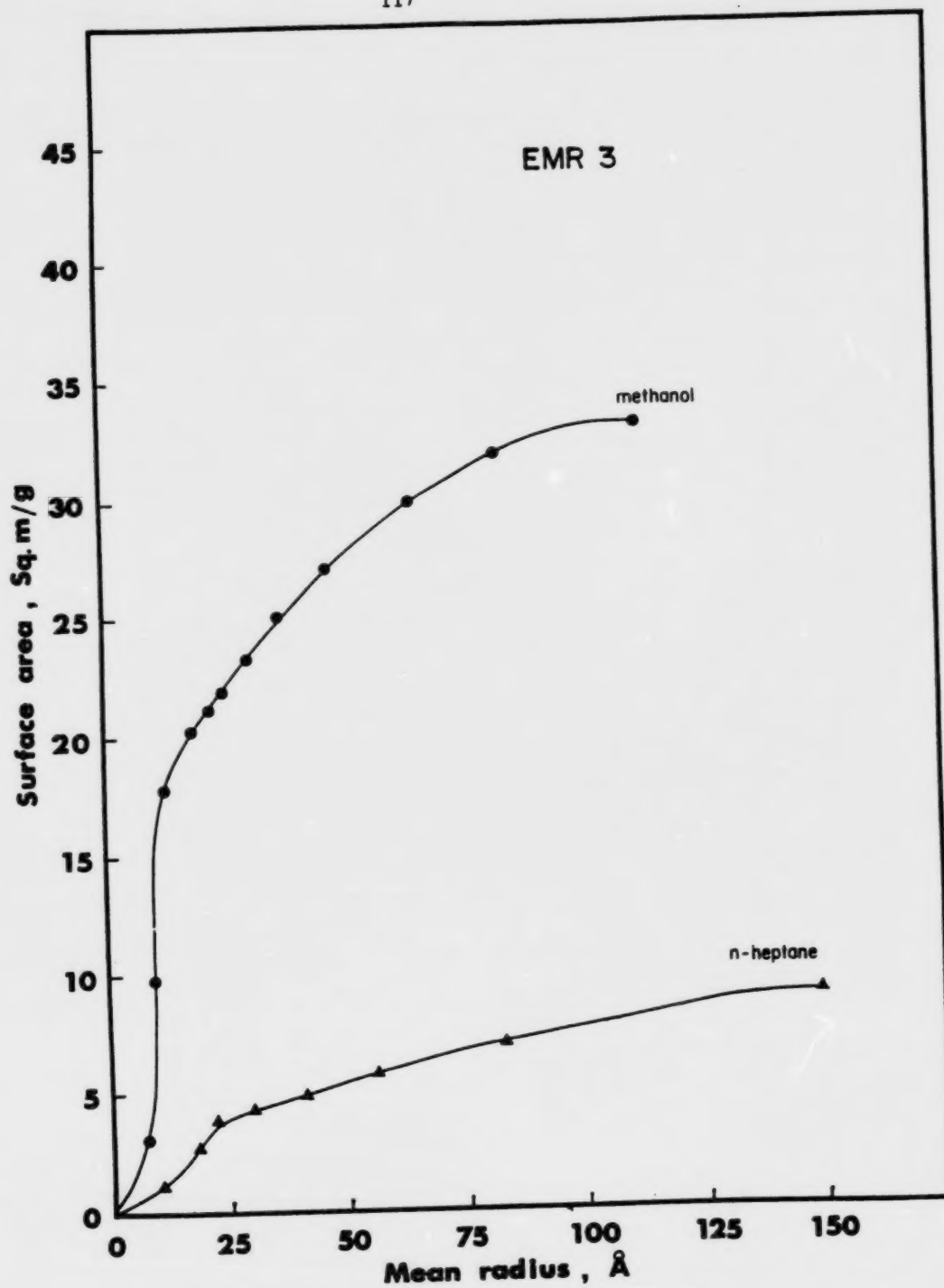


Figure 75 Pore Structure of EMR Sample No. 3

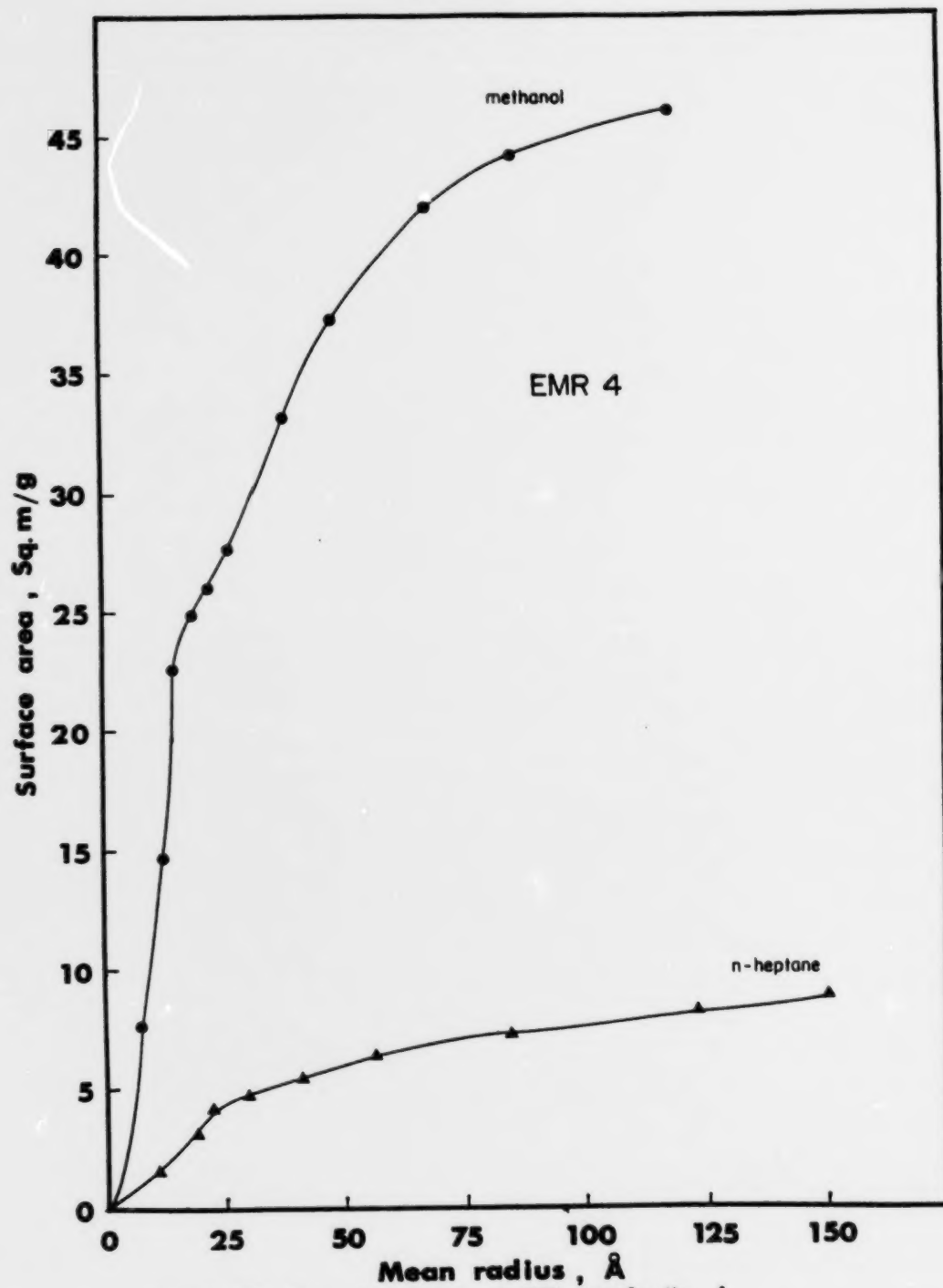


Figure 76 Pore Structure of EMR Sample No. 4

Figure 77 Pore Structure of EMR Sample No. 5

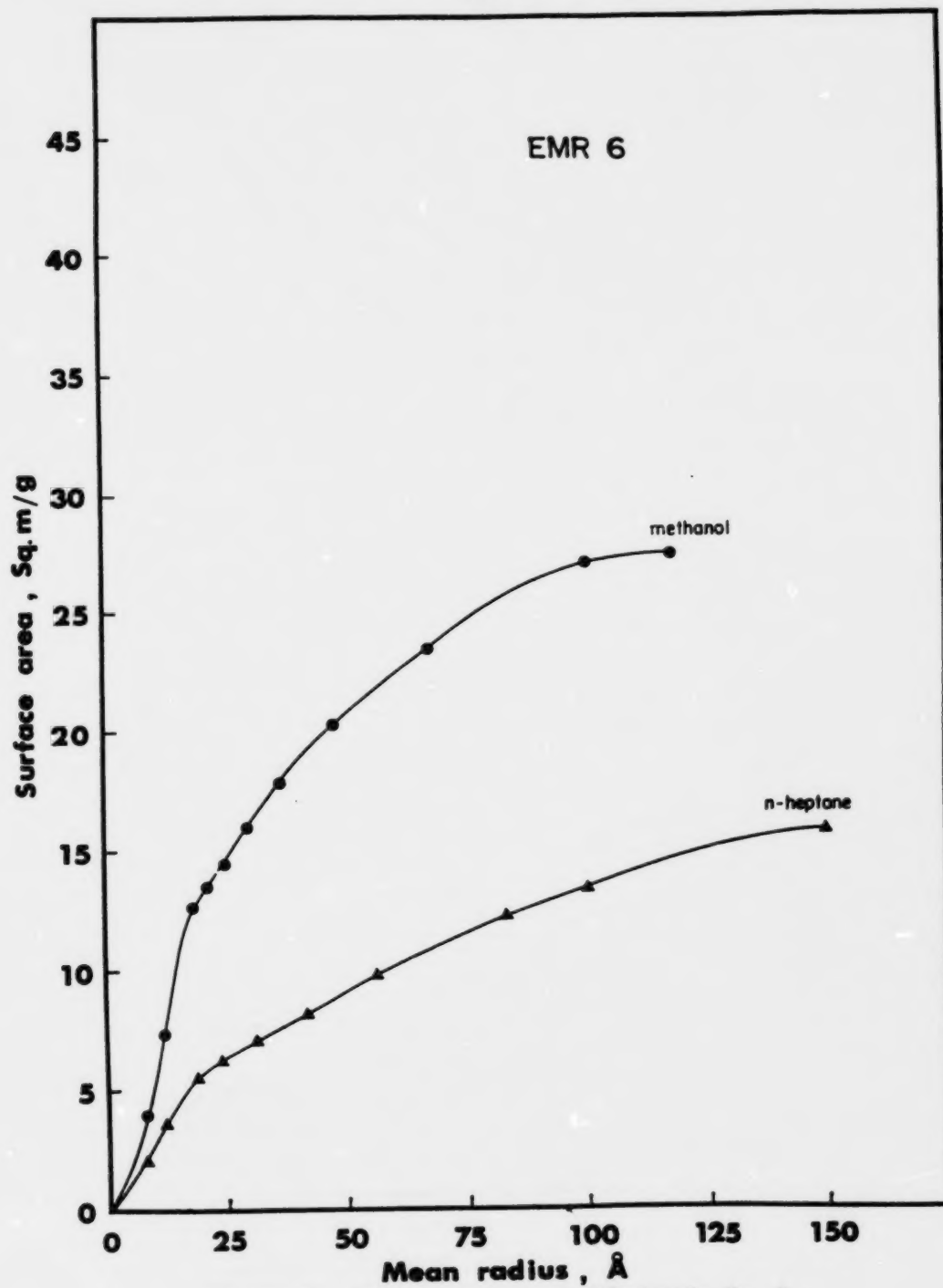


Figure 78 Pore Structure of EMR Sample No. 6

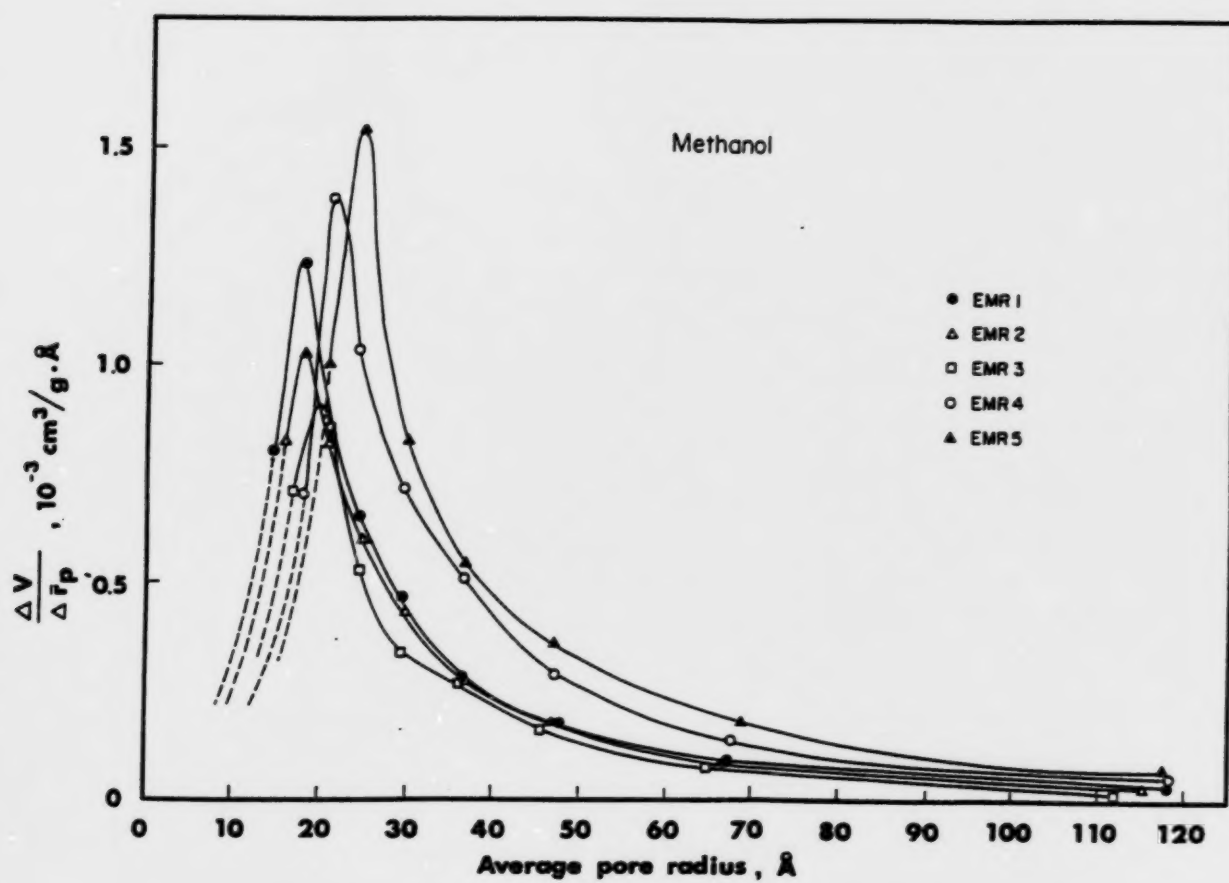


Figure 79 Pore Size Distribution For Western Coal Samples

TABLE 29 Main Pore Structure Parameters

Sample	Total surface area m ² /g	N-HEPTANE				Transitional volume cm ³ /g MESO	Micropore volume cm ³ /g
		1	2	3	4		
METHANOL							
Prince Devco Met.	16.9						
EMR 1	12.1			4.5	0.0206	-	0.0018
EMR 2	9.5	5.0		3.7	0.0214	0.0147	0.0037
EMR 3	11.3	7.6		3.9	0.0200	-	0.0029
EMR 4	9.2	5.3		-	0.0198	-	0.0013
EMR 5	9.0	-		3.4	0.0163	0.0127	0.0041
EMR 6	9.8	6.3		6.3	0.0228	0.00170	0.0055
	15.5	9.2					
METHANOL							
Prince Mine Devco Met.	18.7	12.6		6.1	0.0401	0.0203	0.0094
EMR 1	21.4	14.0		7.1	0.0453	0.0209	0.0107
EMR 2	35.4	15.3		20.1	0.0425	0.0230	0.0123
EMR 3	29.9	14.6		15.3	0.0400	0.0221	0.0098
EMR 4	33.4	12.8		20.6	0.0327	0.0191	0.0097
EMR 5	48.1	24.5		23.6	0.0668	0.0370	0.0179
EMR 6	60.7	24.3		36.4	0.0682	0.0378	0.0189
	27.2	14.8		12.4	0.0404	0.0222	0.0095

III.8 Comparative Evaluation of Coal Wettability Measuring Techniques

Selection of the wettability measuring technique most suitable for the case of coal fines depends on a multitude of parameters, most important of which is its ability to detect small variations in the state of oxidation of coal surfaces. This requires both high reproducibility and relatively high sensitivity to variations in surface characteristics. The technique should also preferably be fast, require little capital investment and easy to use with minimum training. A comparative evaluation of the following techniques was, therefore, undertaken:

1. Wetting time
2. Drop drainage time
3. Capillary pressure due to liquid imbibition in a packed bed of powder
4. Weight gain due to liquid imbibition
5. Minimum pressure required for the formation of a bubble
6. Heat of wetting
7. Vapour adsorption

III.8.1 Sensitivity to Variation in Surface Characteristics

The sensitivity of various wettability measuring techniques to systematic variation in the surface characteristics of coal (stemming from progressive oxidation at 100°C) is graphically depicted in Fig. 80. The results obtained enable the ranking of the various techniques in the following order w.r.t. their sensitivity:

7>6>2>4>1>3>5

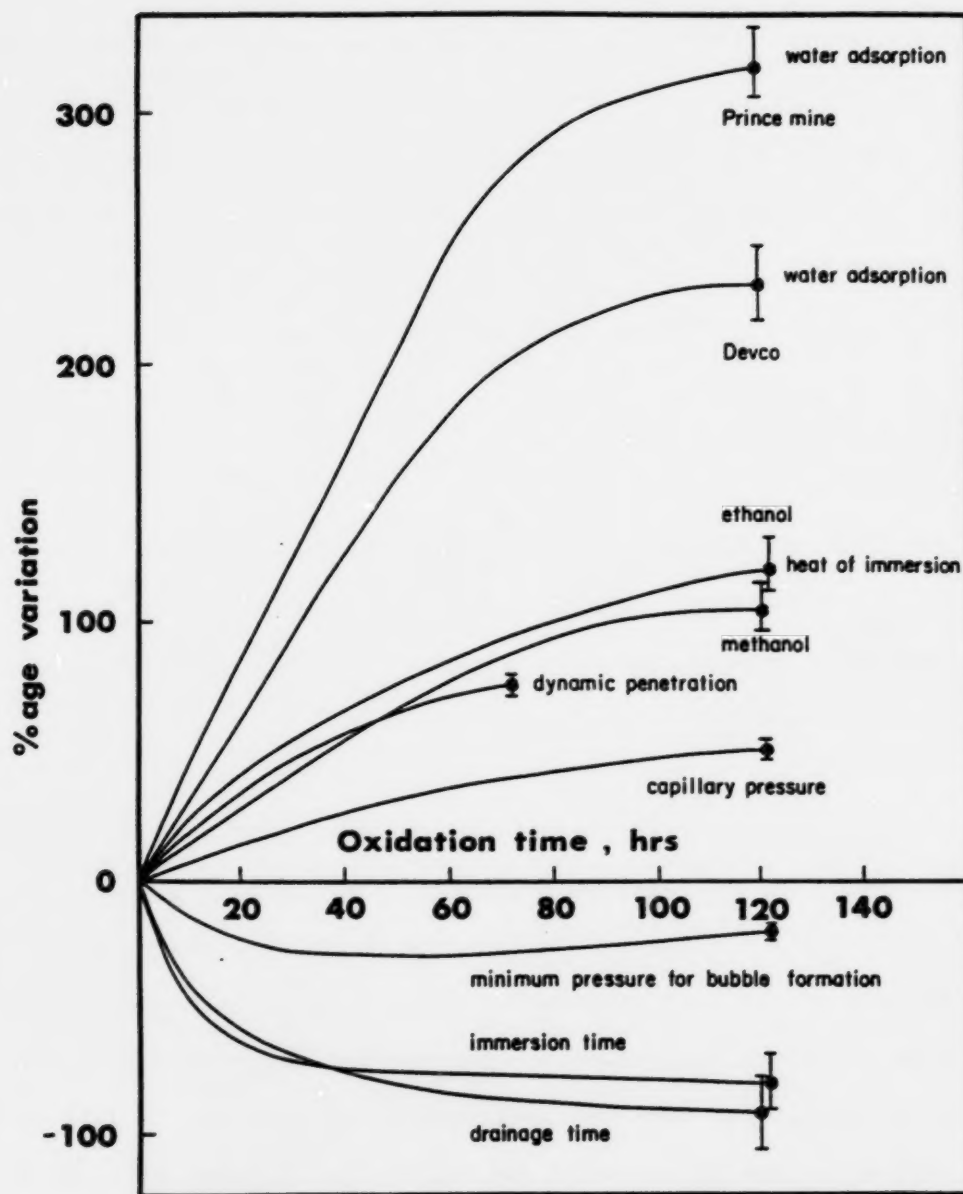


Fig. 80 Sensitivity of Various Wettability Measuring Techniques to the Oxidation of Coal Surfaces

All techniques, with the exception of minimum-pressure and immersion-time, exhibit similar normalized tendencies. The discrepancy observed in the case of the minimum-pressure technique could stem from its reliance on receding contact-angle instead of the advancing contact-angle as is the case with all other tests. On the other hand, no plausible explanation could be presented to explain the higher sensitivity of the immersion-time technique to small changes in the coal's hydrophobicity.

III.8.2 Reproducibility

The reproducibility of various techniques has been dealt with in their respective sections. Emphasis will, therefore, be focused on a comparative evaluation between the technique whose normalized variances are presented in Figures 81 and 82.

In general, a strong correlation exists between the magnitude of the measured parameter and the reproducibility of the corresponding test. Thus, the larger the value of the measured parameter, the better is the test's reproducibility, and vice versa. This suggests an almost constant variance whose value is independent of the surface condition of the coal. On the other hand, drop drainage times present an exception to this rule where no explanation can be presented for the minimum observed after 40 hrs of oxidation.

As is evident from Figures 81 and 82, most wettability measuring

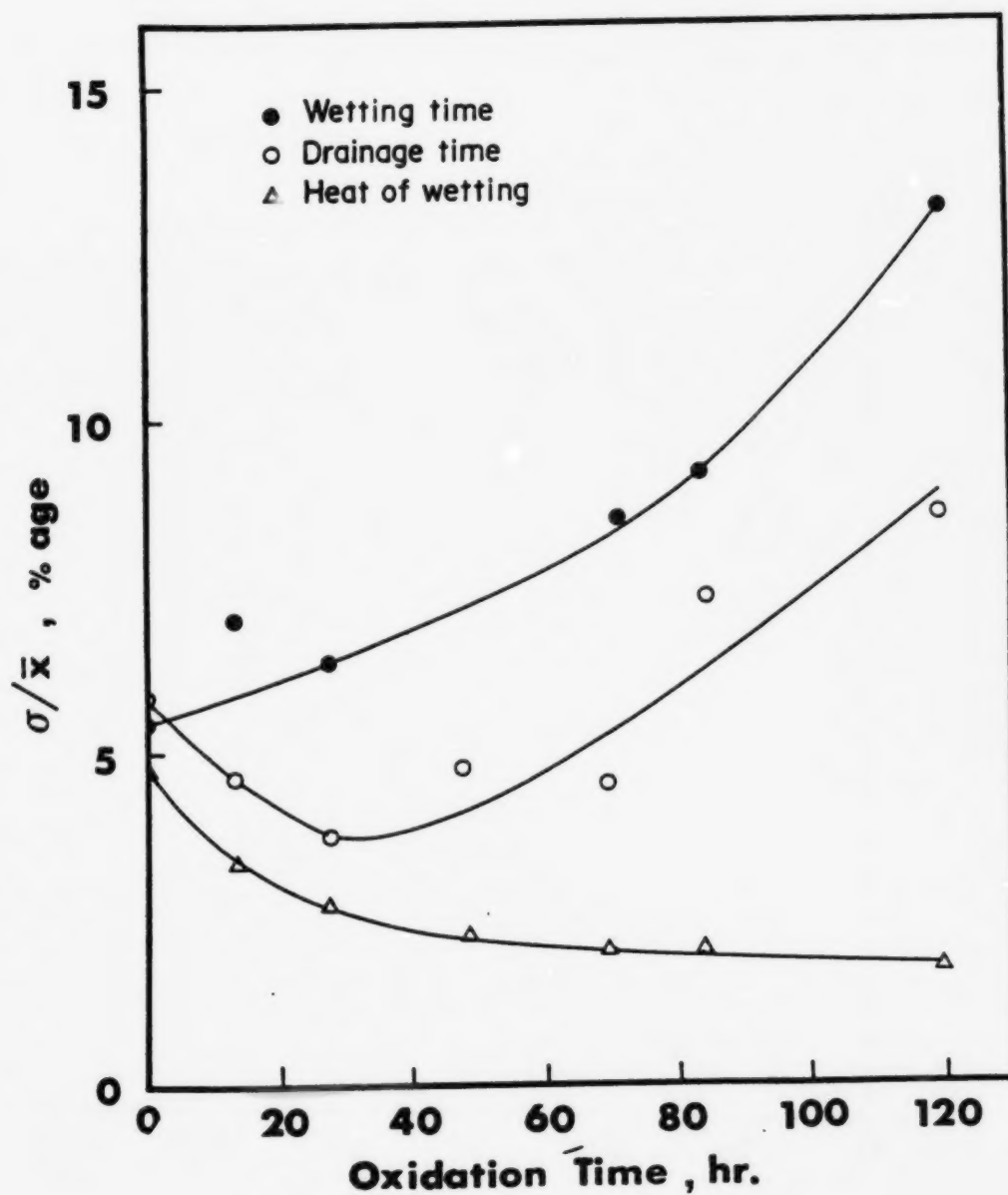


Fig. 81 Effect of Coal Oxidation On the Reproducibility of Wettability Measuring Techniques

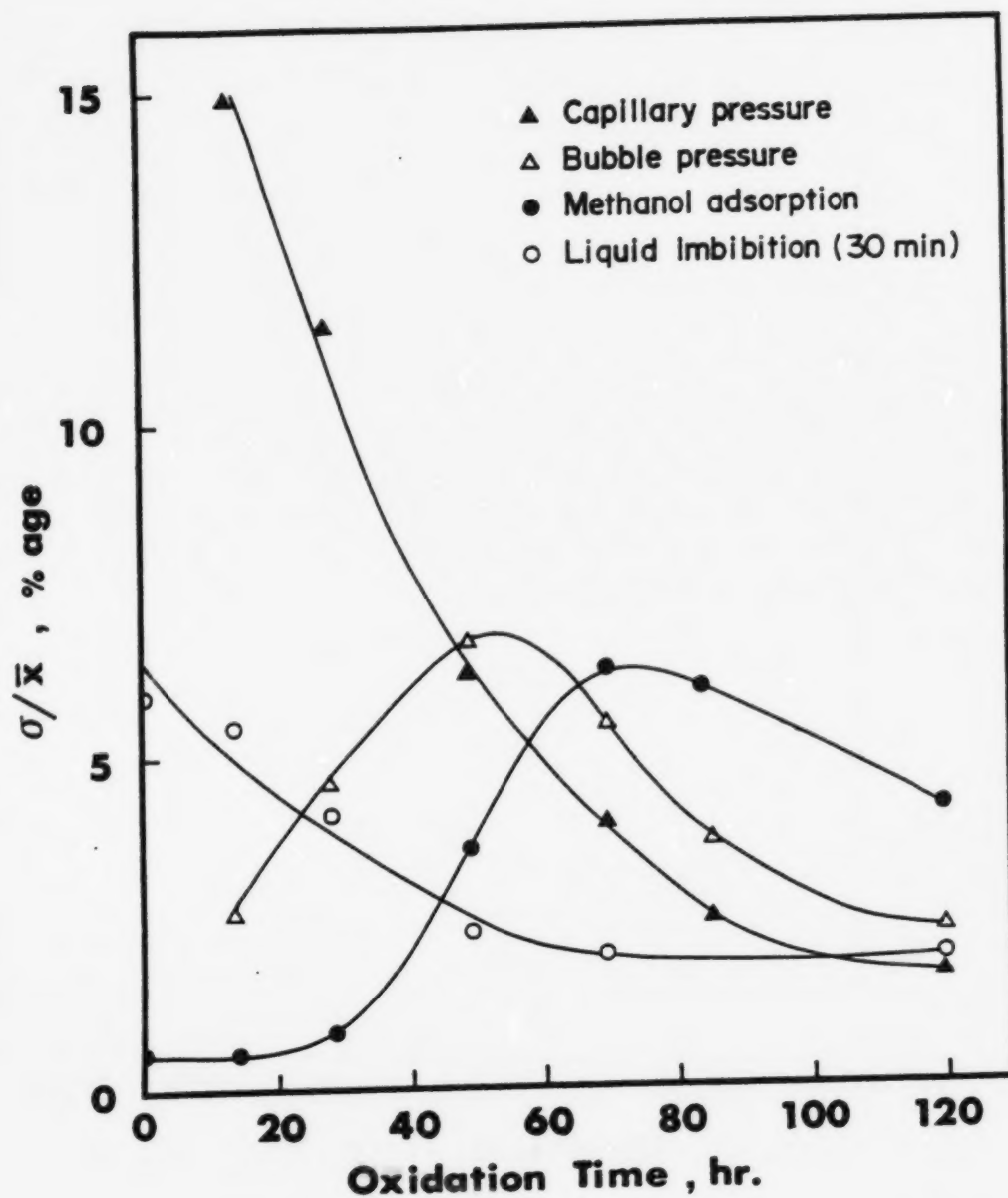


Fig. 82 Effect of Coal Oxidation On the Reproducibility of Wettability Measuring Techniques

techniques have normalized variances of 5% or less and can be further improved by appropriate selection of the wetting solution. The same approach can also be used to overcome the excessively high variances encountered with part of the capillary pressure, liquid imbibition, wetting-time and drop-drainage-time data. Thus, for example, the use of lower methanol concentrations will improve the reproducibility of the wetting-time and drop-drainage-time data when applied in conjunction with very hydrophillic coals (such as those obtained upon prolonged oxidation of coal). On the other hand, use of higher methanol concentrations is expected to improve the reproducibility of the capillary pressure and liquid imbibition techniques when used for measuring the wettability of relatively hydrophobic coals.

III.8.3 Cost and Labour Requirements

A comparative evaluation of the cost and labour requirements needed for evaluating the wettability of coal fines is presented in Table 30. The advantages of simple and inexpensive techniques such as the wetting-time approach, have to be balanced against the extensive training and high labour requirement associated with such approaches. Furthermore, the data generated are rather imperical and can at best yield information about the overall characteristics of the coal surface. On the other hand, sophisticated techniques, such as vapour adsorption, can yield an insight into the distribution of various hydrophobic and hydrophillic active sites on the surface of the coal as well as their energy of interaction with various adsorbates.

Table 30: Cost and Labour Requirements of Various Coal Wettability Measuring Techniques

Technique	Estimated capital requirements \$	Testing time	Min. No. of Replicates	Remarks
Wetting time	1,000-1,500	20-30 min (excluding screening)	4-5	-Off-shelf equipment -Does not lend itself to automation -Extensive operator-training necessary
Liquid imbibition in a packed bed	5,000-7,000	1 hr	3-4	-Most of the cost attributed to electronic balance (a multipurpose laboratory item) -Minimal special-construction items -Fairly automated
Capillary pressure due to liquid imbibition	4,000-5,000	2-4 hrs	4-5	-Average operator training -Special construction
Minimum bubble pressure	1,500	1 hr	3-4	-Average operator training -Low reproducibility -Specially constructed setup -Presently labour intensive but lends itself to automation
Drop drainage-time	2,000-3,000	5 min + 15 min for pellet preparation	2-3	-Average training period -Standard off-shelf components -Rugged test -Minimal training -Most suitable for field testing
Heat of wetting	5,000-10,000	2 hrs (excluding degassing)	2-3	-Off-shelf equipment -Fairly automated -Minimal training but sample degassing crucial
Vapour adsorption	60,000-70,000	2-3 hrs	1-2	-Off-shelf unit is rather expensive, but adapted modern GC units may be used -Fully automated -Highly-trained operator needed

Such an approach, however, necessitates high capital investments and highly trained personnel in order to interpret the data. High investment costs associated with the purchase of specialized equipment may be reduced by modifying gas chromatographs (an instrument present in most laboratories) to enable measurement of surface characteristics.

III.9 Coal Flotability

The role surface characteristics play in determining the recovery achievable while floating coal is strongly dependent on particle size. Thus, as can be seen from Figures 83 and 84, the influence of surface characteristics is most prominent for particles of large sizes. An explanation for such a behaviour has recently been given by Trahar (78) and is based on the concept that the overall probability of flotation can be related to the three most important subprocesses as:

$$P_f = P_c \times P_a \times (1 - P_d)$$

where P_f , P_c , P_a and P_d refer to the probabilities of flotation, collision, adherence and detachment.

The probability of particle-bubble collision has attracted much attention which has recently been summarized by Jameson et al (79) and Sablik (80). Although the exact form of the relation between collision frequency and other variables has not been established beyond dispute, there is agreement that P_f is related to particle and bubble diameters, particle and liquid densities, liquid viscosity and relative particle-bubble velocity. No term relating to

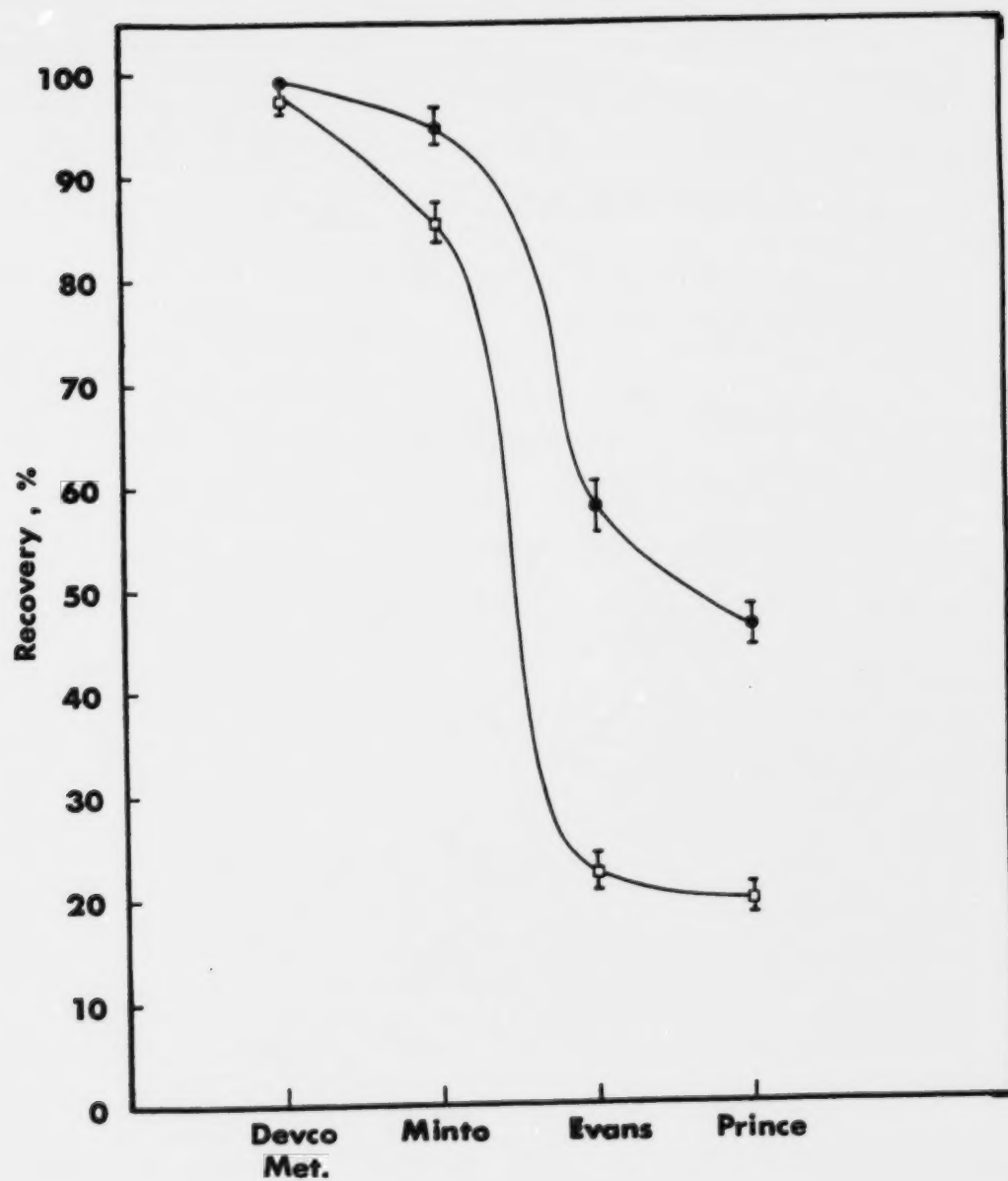


Figure 83 Effect of Particle Size and Surface Characteristics on Flotation Recovery (Maritime Coals)

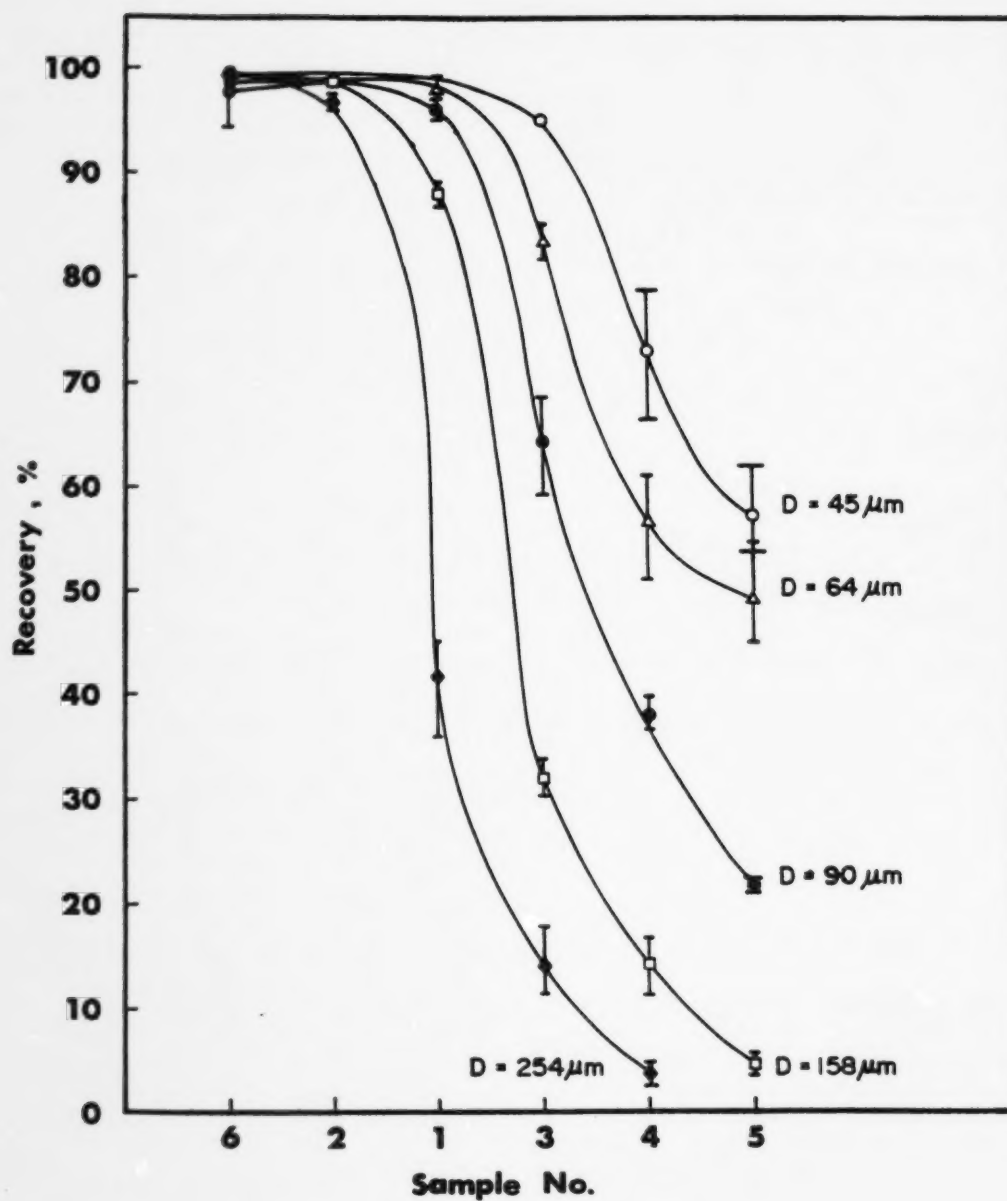


Figure 84 Effect of Particle Size and Surface Characteristics On Flotation Recovery (Western Coals)

the contact angle appears in any of the expressions for P_C , which should, therefore, not be significantly influenced by the chemical nature of the flotation system (except indirectly through the population densities of the bubble and the relative electrical charge of particles and bubbles).

The variables which influence the probability of adherence, P_a , are less well understood for the problems are complex and the variables interrelated. Furthermore, although it is possible in concept to distinguish between collision and adherence, there is a real difficulty in knowing where one ends and the other begins. In qualitative terms, P_a can be considered to be inversely related to the induction time, which is the time needed for thinning and rupture of the film between the particle and bubble. If the induction time is less than the particle-bubble contact time, adherence occurs. Experimental results suggest that induction time is inversely related to collector concentration and directly related to particle size so that relatively small increases in particle diameter can lead to large increases in induction time.

The third term $(1-P_d)$ is dependent on the forces of adhesion between particle and bubble which in turn is directly related to contact angle, interfacial tension and inversely related to particle size (79). Several attempts at quantifying the form of the relationship between the various parameters are presently underway, but the situation is complicated by the strong role of the hydrodynamic shear forces.

In summary, the above relationships can be expressed as:

$$P_c \propto f(d)$$

$$P_a(1-P_d) \propto f'(\text{SURFACE PROPERTIES})/f''(d)$$

The recovery curves will, therefore, be a compromise between P_c on the one hand and $P_a(1-P_d)$ on the other, so that there is a size range where the recovery reaches a maximum. For strongly hydrophobic coal $P_a(1-P_d)$ will approach unity and the flotation rate will be primarily determined by P_c which increases with particle size. Such interpretation is in accord with the observation that the cumulative recovery of fines is determined more by the available flotation time than by the chemical environment since the critical level of hydrophobicity is easily exceeded for such particles (78).

On the other hand, for relatively large particles of less hydrophobic nature, the recovery rate is mainly determined by $P_a(1-P_d)$ and is, therefore, strongly affected by surface characteristics and is reduced with increasing particle size. Such problems are reported to occur during the beneficiation of several difficult-to-float coals. The process of stage-wise addition of reagents has been proposed as a promising means for overcoming this difficulty (81).

III.10 Relationship Between Surface Characteristics of Coal and Its Flotability

Several attempts have been made to correlate the flotability of coal with its intrinsic characteristics (82-87) and were met with varying degrees

of success. This topic is discussed in a separate report (88) and one of the major conclusions attributes the lack of success to the attempt of various investigators to use indirect measures of surface characteristics as an indication of the coal's "wettability". Furthermore, the recent work of Gutierrez and Aplan (86, 87) suggests that various wettability measuring techniques are not equally capable of predicting the flotation characteristics of coal, while Fowkes et al. (89) report that depending on the wettability measuring technique (advancing or receding angle) one may be measuring the most hydrophobic, or the most hydrophilic, parts of the surface.

A comparative evaluation of the capability of various wettability measuring techniques to correlate coal flotability data was, therefore, undertaken and the results are presented in figures 85-93. Flotation results were not changed to account for variation in ash content (with consequent variation in surface hydrophobicity and particle density) with particle size; but as can be seen from Fig. 10 this is expected to be quite pronounced only in the case of samples No. 3 and 5.

As can be seen from Figures 85-87, coal recovery was found to correlate rather poorly with its primary intrinsic properties (C, O₂ and moisture); with the scatter being highest the larger the particle size. Amongst the three parameters considered, moisture content was found to yield the best correlation coefficient but the recovery is somewhat insensitive to variations in moisture contents larger than 1%, while on the other hand it is exceedingly sensitive to variations in the range 0-1%. Better success was achieved when

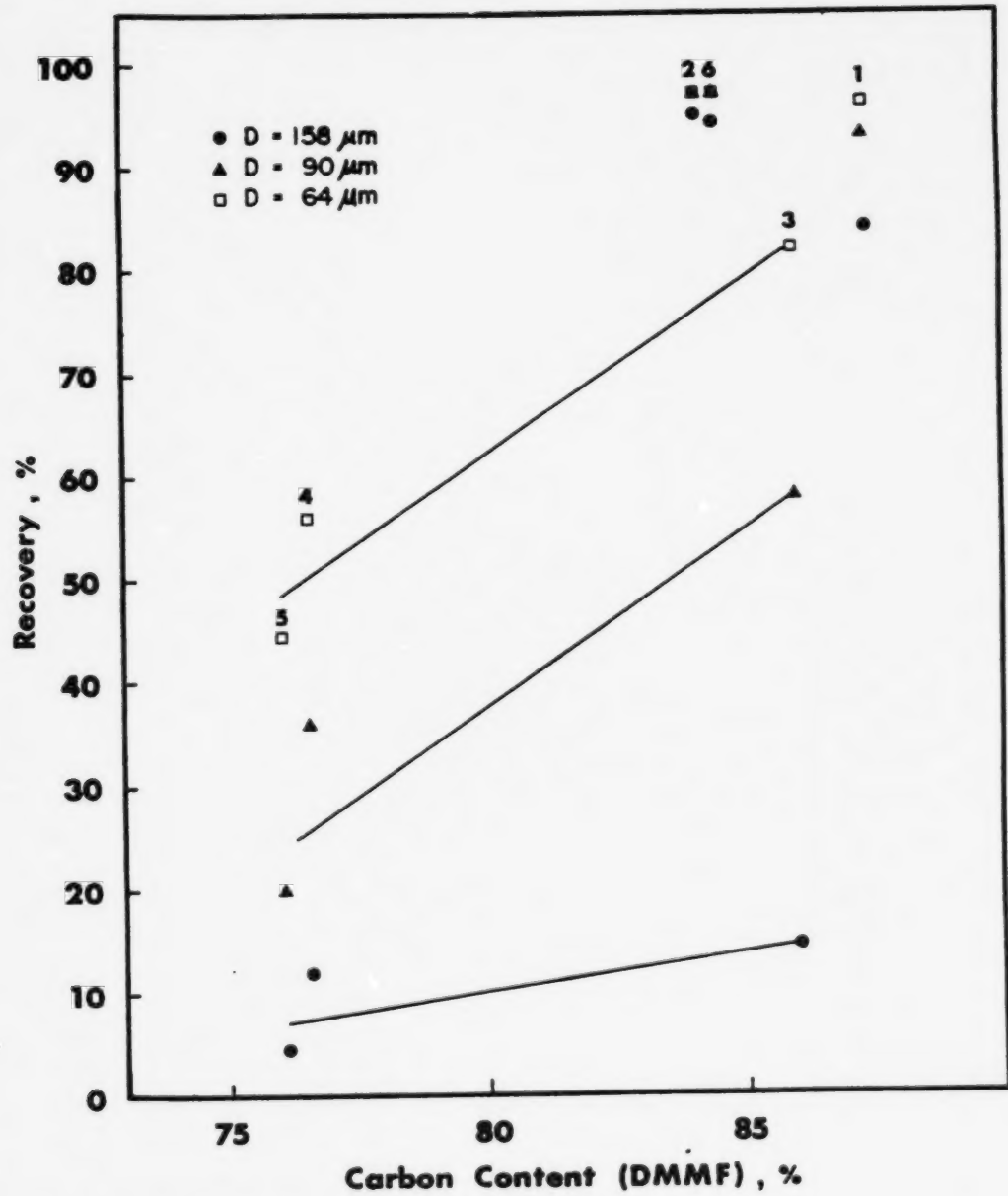


Figure 85 Relationship between the carbon content of coal and its flotability

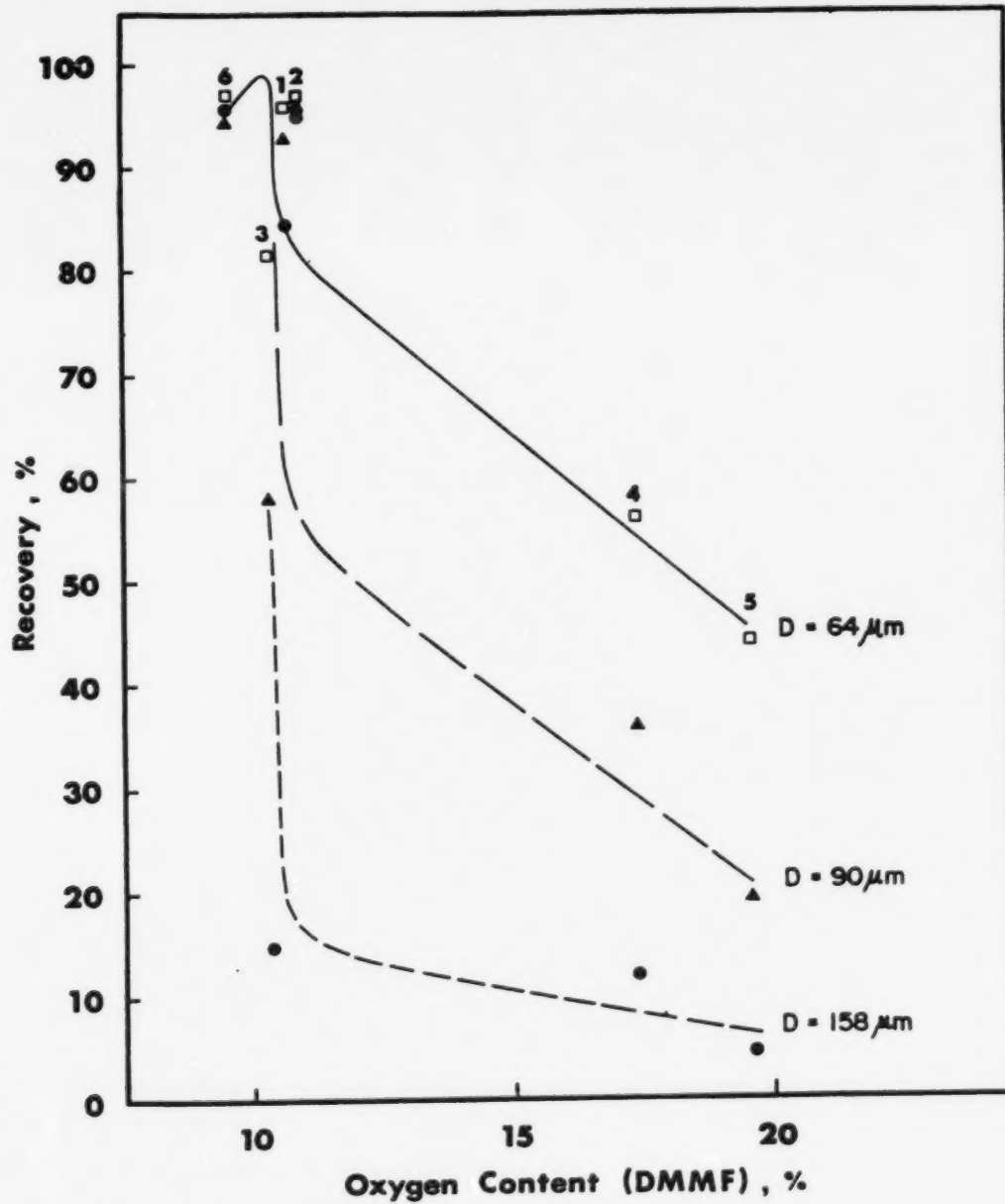


Figure 86 Relationship between the oxygen content of coal and its flotability

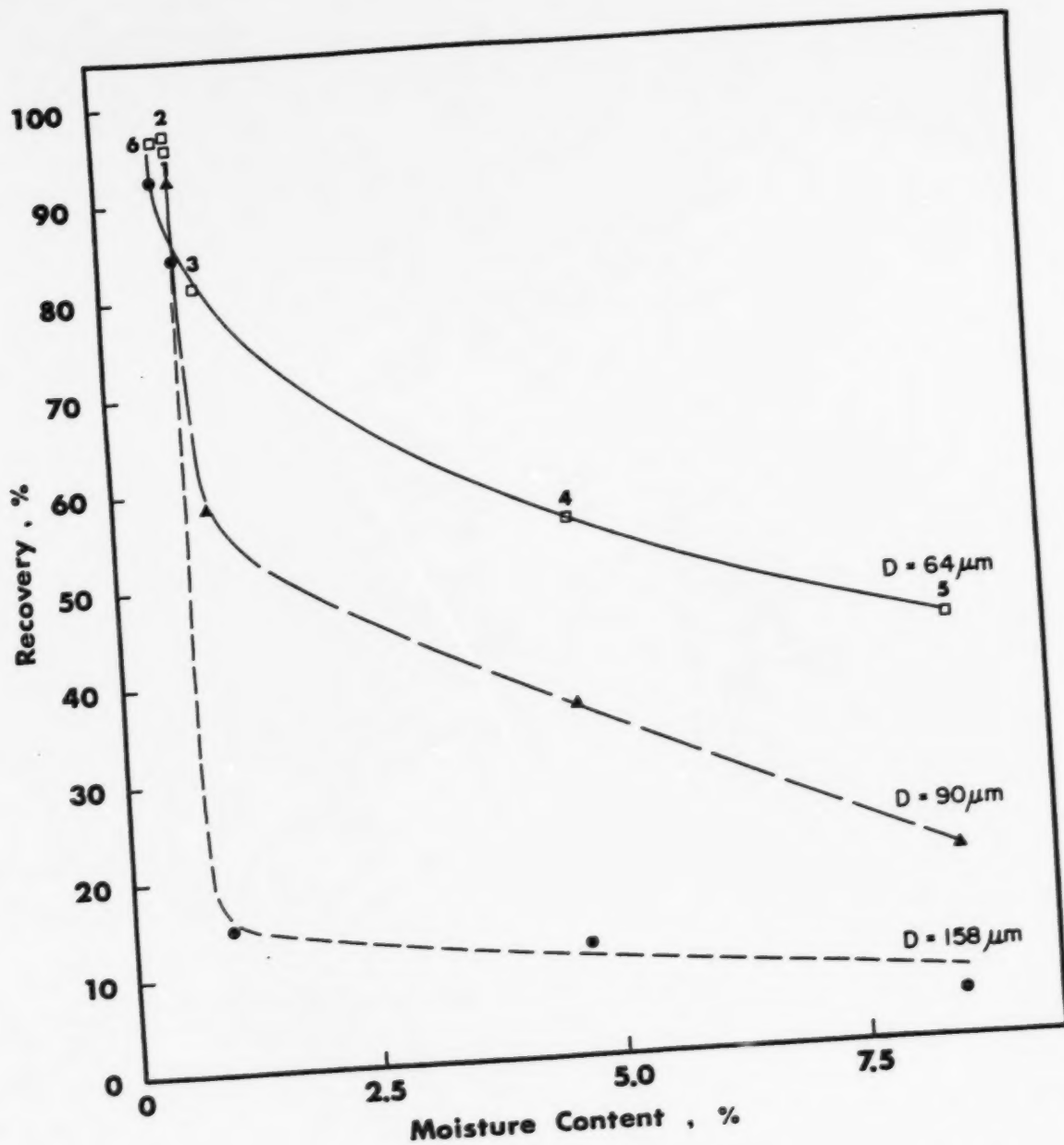


Figure 87 Relationship between the moisture content of coal and its flotability

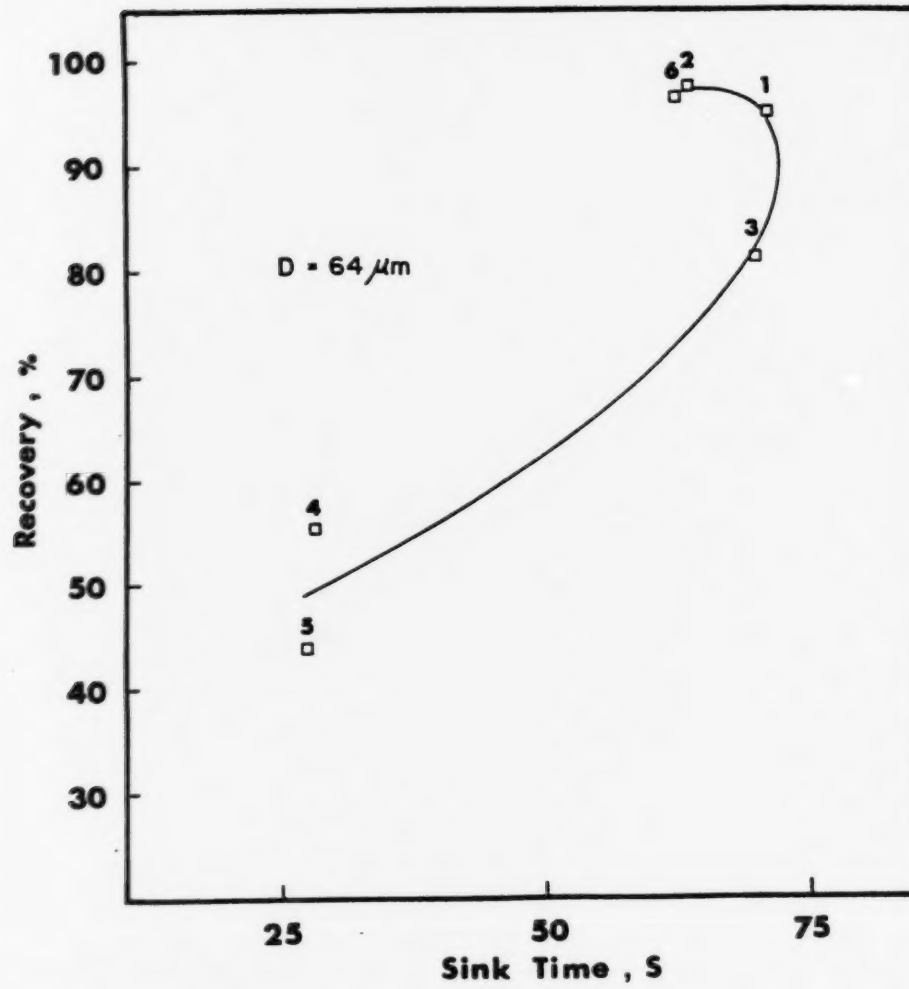


Figure 88 Effect of coal wettability, as determined by the sinking-time technique, on its flotability

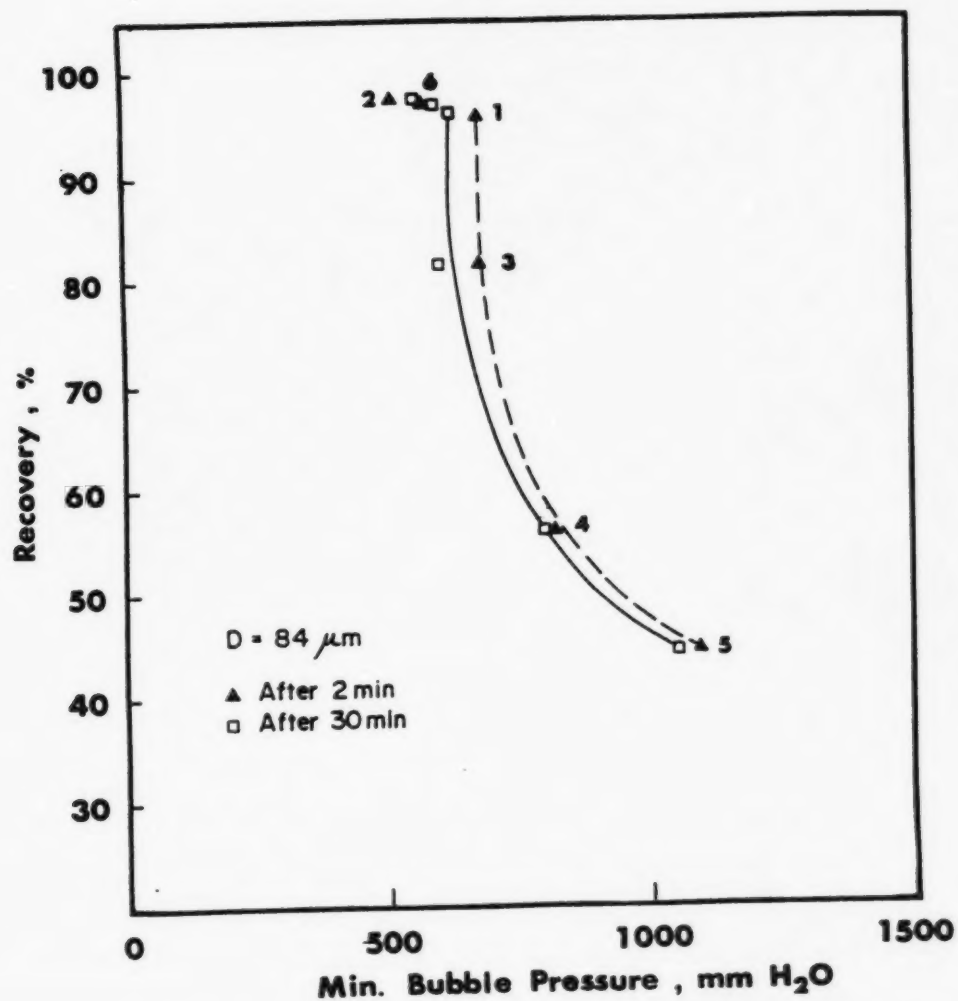


Figure 89 Effect of coal wettability, as determined by the minimum bubble pressure technique, on its flotability

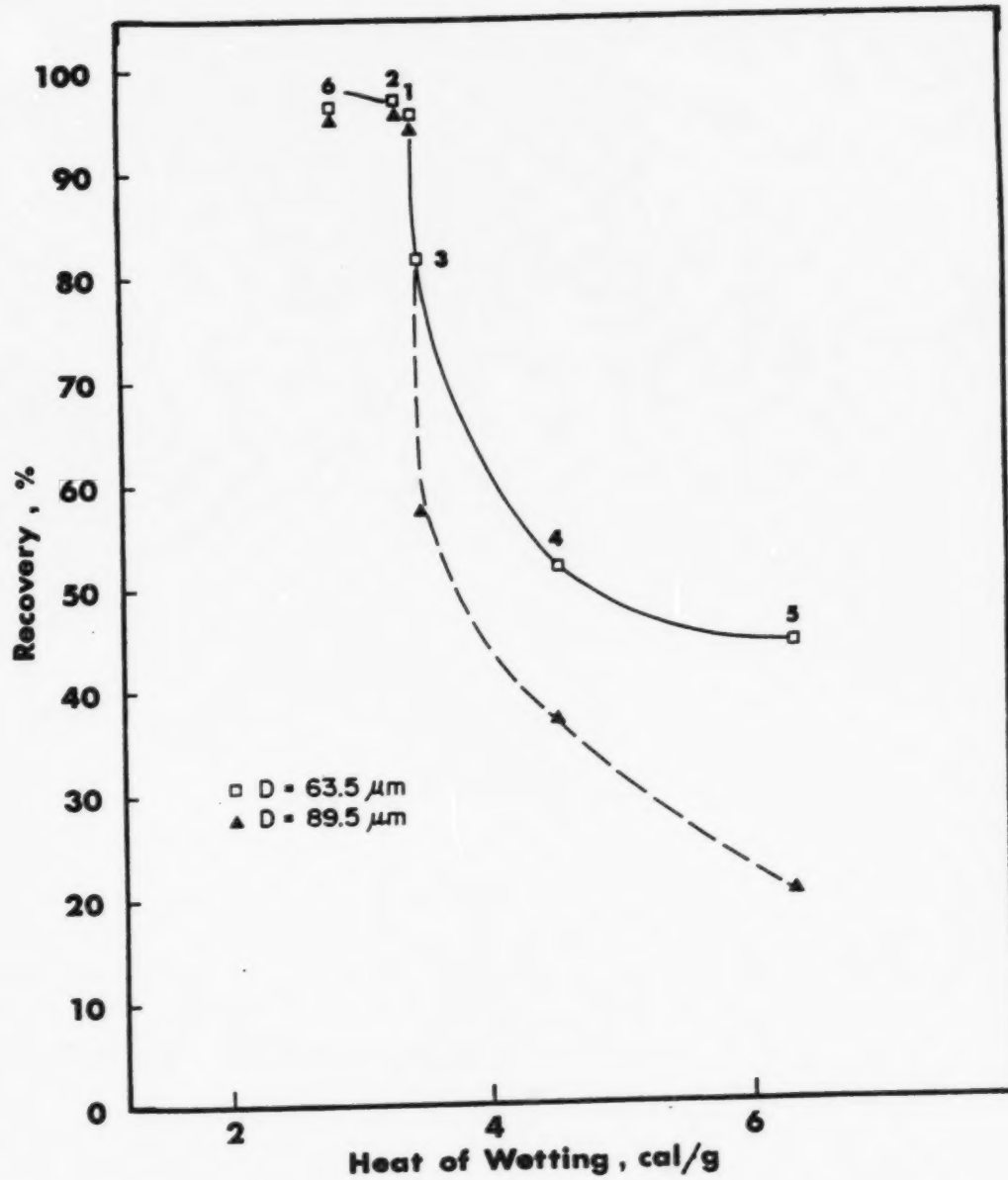


Figure 90 Effect of coal wettability, as determined by the heat of wetting technique, on its flotability

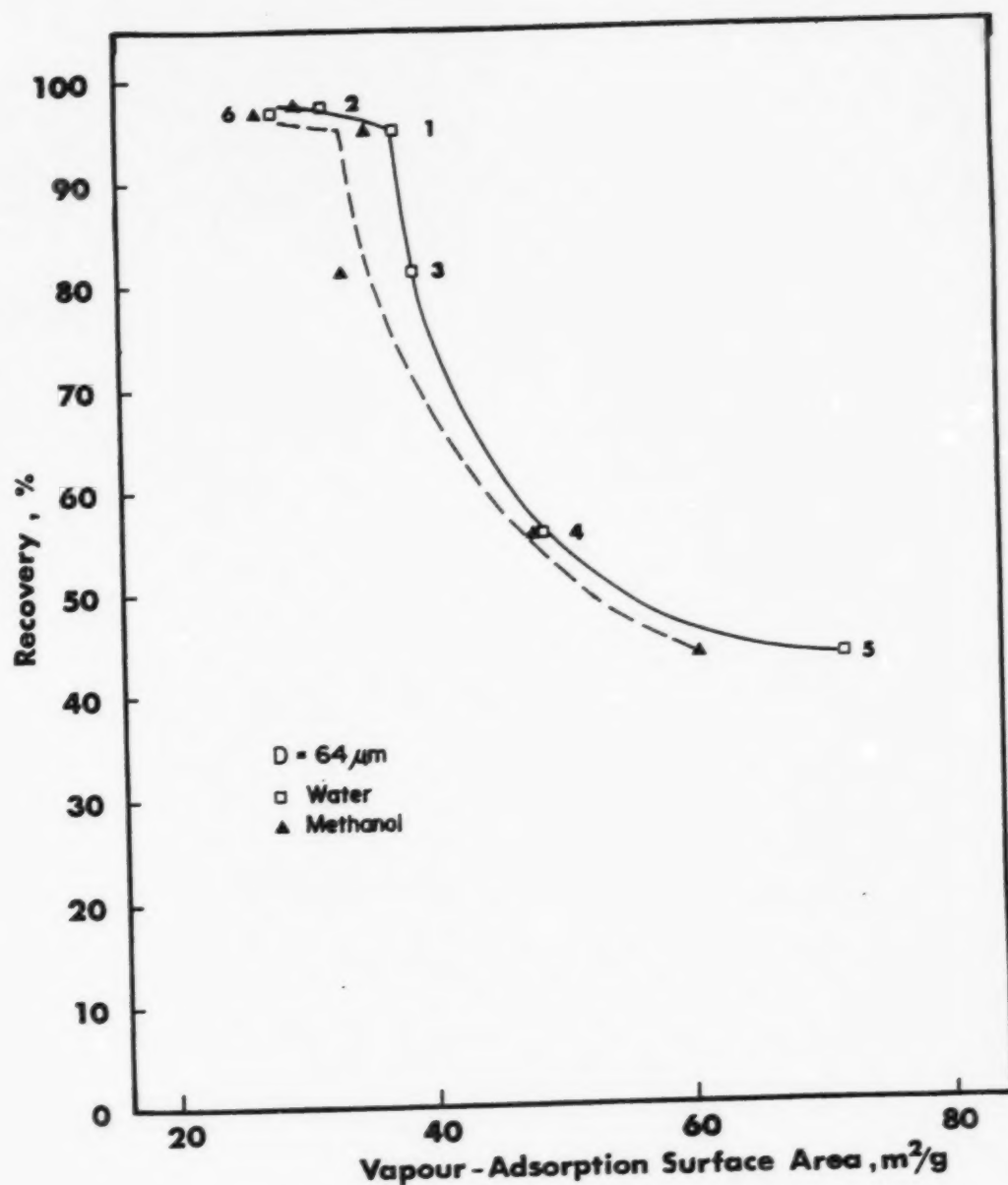


Figure 91 Effect of coal wettability, as determined by the vapour adsorption technique, on its flotability

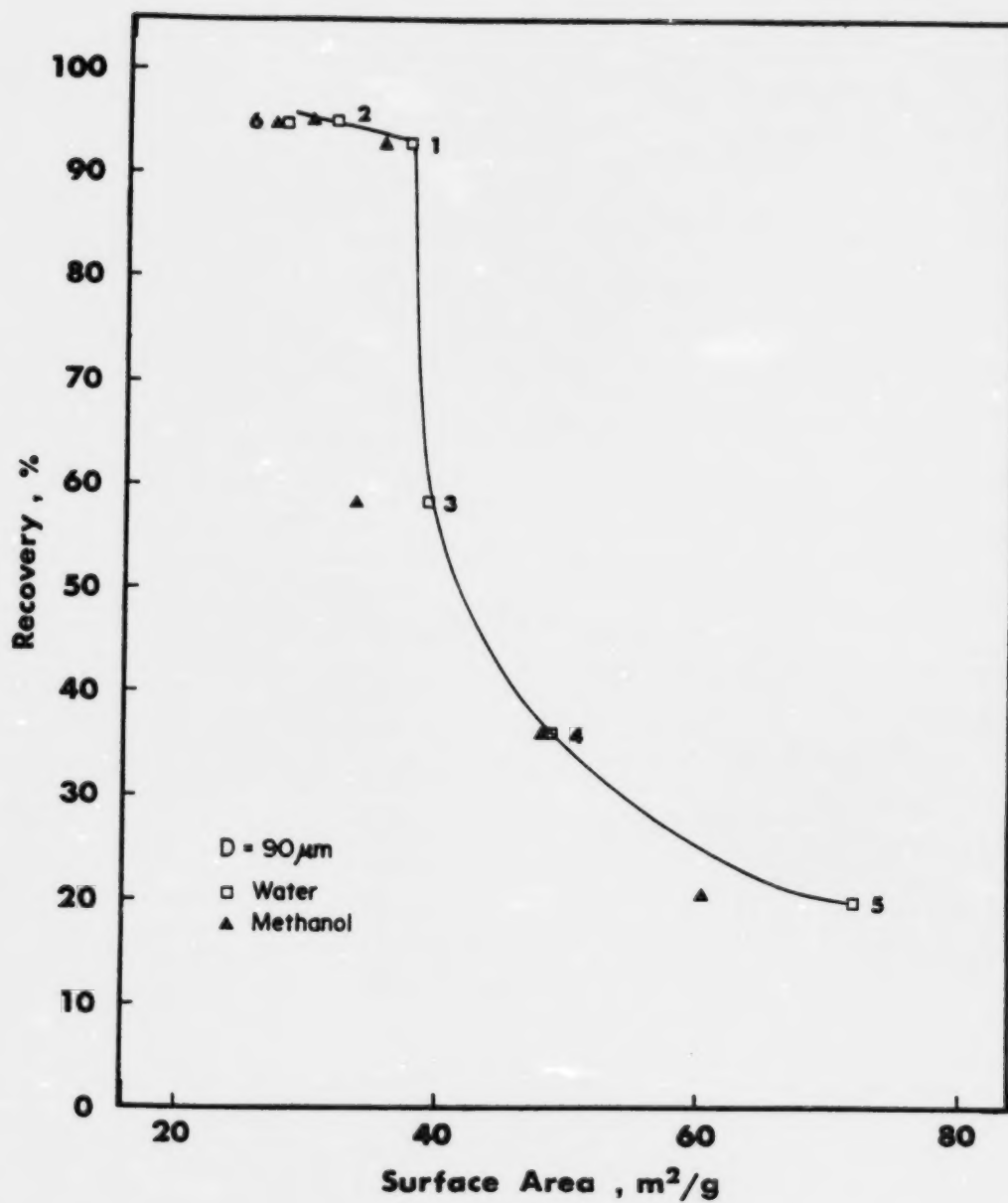


Figure 92 Effect of coal wettability, as determined by the vapour adsorption technique, on its flotability

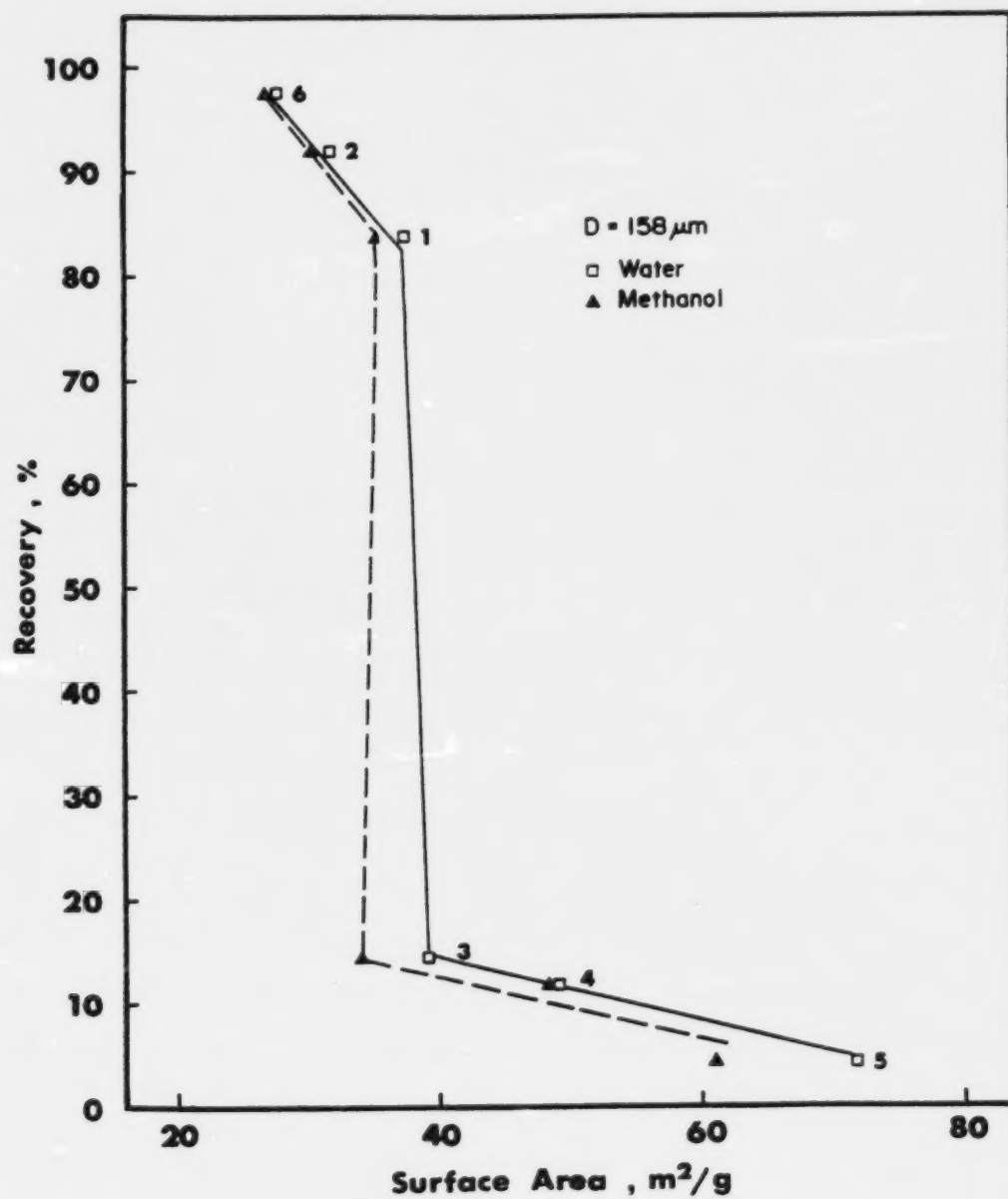


Figure 93 Effect of coal wettability, as determined by the vapour adsorption technique on its flotability

wettability parameters such as minimum bubble pressure, heat of wetting and vapour adsorption was utilized (Figures 88-93). Utilization of sink-time was, however, found to exhibit an inversion at wetting times of 72 s/g for which no physical interpretation can be presented.

The data shown in Figures 89-93 clearly indicate that the six coal samples (EMR 1-6) can be classified into two distinct groups according to the effect surface characteristics have on flotation recovery. Thus, for instance, the "wettability" of coal samples 5, 4 and 3 play an important role in determining the extent to which the thermal content is recovered while beneficiating it. On the other hand, recoveries of coal samples No. 6 and 2 are only marginally affected by its surface characteristics whereas coal sample No. 1 is a border-line case in between the two grouping. This phenomenon can be easily explained by considering the attachment forces between the bubbles and air bubbles, as well as the tendency towards the rupture of such attachment resulting from the interaction between the coal particles and the turbulent field in the cell.

For small coal particles having highly hydrophobic surfaces the forces of attachment are rather high and often exceed the turbulent-interaction forces favouring rupture. For such cases, variations in surface characteristics are expected to exert a minor influence on flotation recovery. On the other hand, as coal hydrophilicity increases (due to weathering or decrease in rank) a point is reached beyond which the forces of attachment between coal particles and bubbles are no more capable of resisting the turbulent disruptive forces

and the recovery henceforth becomes more sensitive to surface characteristics. The point of transition is, therefore, expected to be strongly dependent on the hydrodynamic condition (turbulent structure) prevalent in the flotation cell and may vary with mixing intensity, aeration rate as well as cell type and scale. This phenomenon is particularly evident when the "wettability" is characterized by the surface area as determined by vapour adsorption (Fig. 91-93), where the demarkation between the two regions increases with increasing particle size. The sensitivity to variations in surface characteristics was also found to be maximum for the case of hydrophillic coals when particle sizes are small, whereas the opposite is true in the case of more hydrophobic coals.

The relationship between coal recovery and its surface area (as determined by the adsorption of highly polar compounds such as water and methanol) is influenced by two independent factors, namely variation in pore structure with rank as well as variation in the surface concentration of various polar active sites.

Progression of the coalification process (90) generally results in the reduction of the oxygen-containing functional groups as well as the progressive transition from an open structure, into a liquid structure and ultimately into anthracitic structure (Fig. 94). This is generally associated with a reduction in the surface area (91, 92) and the data obtained on several Maritime coals confirm this phenomenon (Figure 95). It is startling, however,

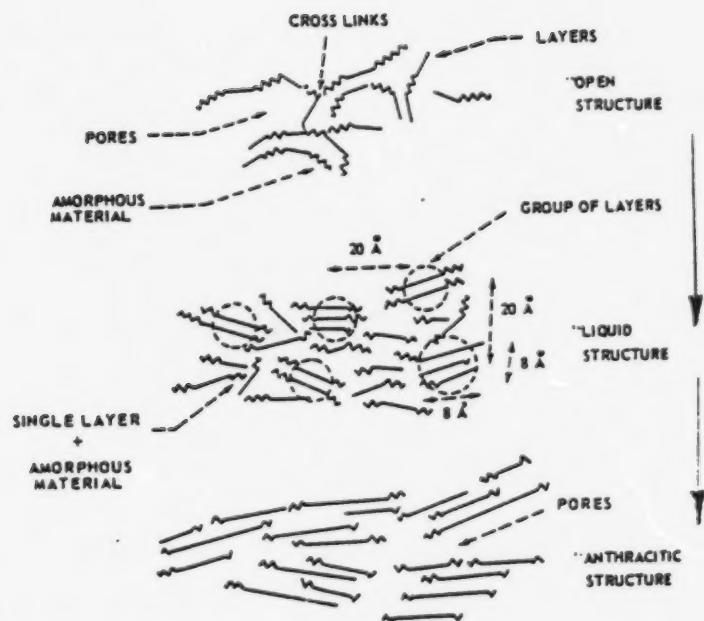


Figure 94 Schematic Representation of the Progressive Transformation In Coal Structure (90)

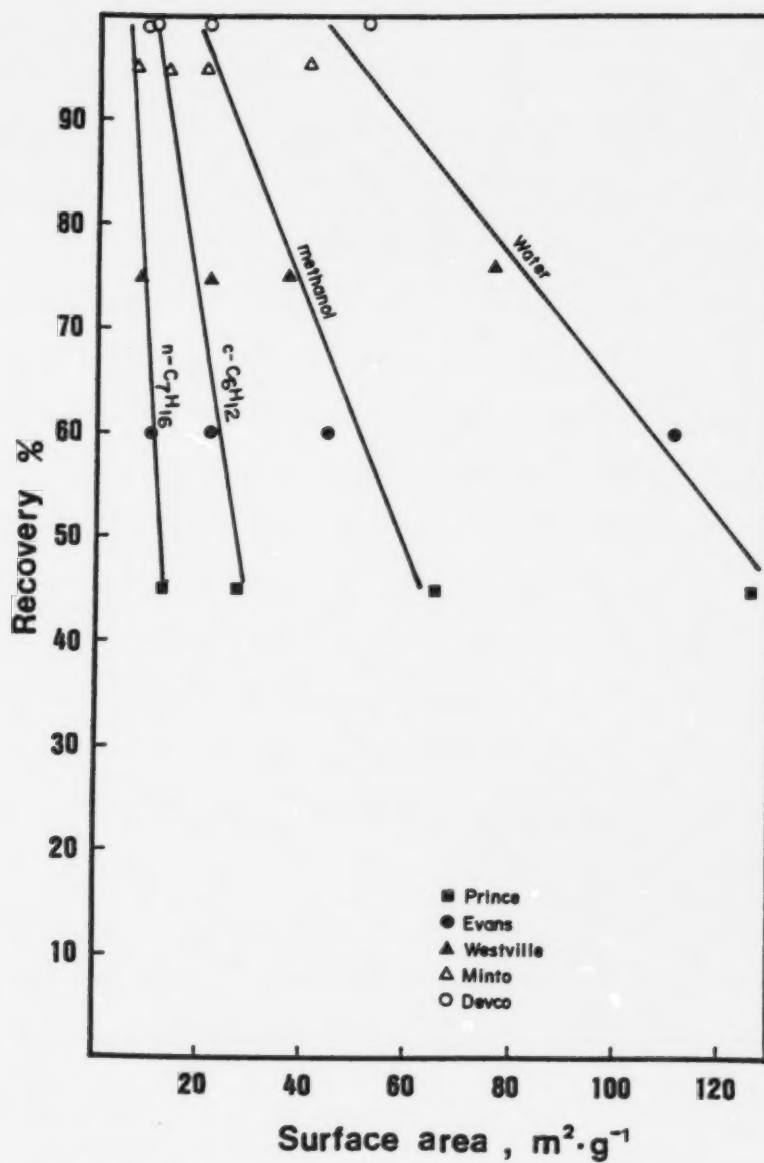


Figure 95 Effect of coal Metamorphosis On Its Surface Area (Maritime Coals)

to notice that the same coal sample could possess a large number of internal-surface-area values depending on the type of adsorbate tested. This phenomenon is commonly encountered in adsorption measurements of coal and has been recently reviewed by Mahajan (92). It can be partially attributed to differences in swelling and accessibility of the pore structure. However, judging by the characteristics of the adsorbates listed in Table 31, it is difficult to explain the data reported in Figure 95. Furthermore, the findings obtained by systematically oxidizing various coal samples (Section III.7.1) depict progressively increasing surface areas measured using highly polar adsorbates (such as methanol and water), whereas the surface area measured using slightly polar adsorbates remain almost constant or decrease slightly. These findings can only be explained on the basis of special interaction between the various adsorbates and the surface of the coal. The nature of this interaction appears to be dependent on the molecular structure of the adsorbate and the chemical nature of the surface, and may, therefore, be influenced (in both the positive and negative sense) by the alteration in the chemical composition of the surface associated with mild oxidation, weathering or metamorphosis. Such transformations explain the observations made during the early stages of this investigation (93) where the retention times for most adsorbates was found to increase with increasing extent of oxidation whereas the opposite trend was obtained using Acetone.

Table 31: Characteristics of Adsorbates Tested

	Molecular Area ($\text{\AA}^2$)	Solubility Parameter (MP_a) ^{1/2}
N-HEPTANE	40.6	15.2
C-HEXANE	34.0	16.9
METHANOL	18.1	29.7
WATER	10.6	48.0

All the above mentioned discrepancies can be reconciled by considering the heterogeneity in the nature of the coal's surface (94). The surface of the coal is considered to have a number of active sites that interact with a particular adsorbate with the energy of interaction being described by the site-energy distribution function. The latter is very strongly affected by the nature of the active site, that of the adsorbate as well as the temperature and pressure at which adsorption takes place. This concept has long been used in the field of catalysis with great success (95) but appreciation of the highly heterogeneous nature of coal is only beginning to emerge (86, 87).

If we now apply the concept of active sites and site-energy distribution functions to the case of coal, one can expect a gradual increase in the number of active sites per unit surface area as the coal undergoes progressive oxidation. Furthermore, site-energy distribution functions may shift towards higher values until an equilibrium distribution function is reached whose shape and average value may be strongly affected by the temperature and other environmental conditions under which coal is oxidized. This can be clearly seen by comparing the data for heat of wetting by methanol for naturally occurring and synthetically oxidized coals (Figures 48 and 49). The concept of active sites can also explain the preferential adsorption tendency of different compounds as well as the high sensitivity of the distribution coefficient to slight variations in the pH value (96).

The overall wettability of a heterogeneous coal surface will be determined by a balance between the oleophilic sites, to which relatively non

polar organic materials tend to adsorb, and the hydrophillic sites to which water, ions and other highly polar compounds are attracted. In the absence of detailed information about the site-energy distribution functions for both groups, one may use a number-ratio of the oleophillic to hydrophillic active sites (HLR) in order to express the overall surface characteristics of the coal. It is important, however, to select appropriate adsorbates and adsorption temperatures in order to yield HLR values that have practical significance.

Variations in the pore structure of coal (volume of micro, meso and macro pores) are generally expected to result in minor alteration of the density of coal particles, and are consequently expected to exert little impact on coal flotability. On the other hand, the surface characteristic of coal is expected to play a rather significant role. Determination of the HLR value for any particular coal overcomes the difficulties associated with variation in surface area with rank and is, therefore, expected to yield a better measure of its surface characteristics.

Attempts at using water vapour adsorption as an indicator of the hydrophillic sites (Figure 96) was less successful in correlating flotation recovery than was the case with methanol (Figure 97-98). Within the limited range of adsorbates tested, it is, therefore, proposed to use HLR values determined from the adsorption results of methanol and n-heptane. Applying this concept to the case of Maritime coals resulted in extremely good correlation of the data (Fig. 100).

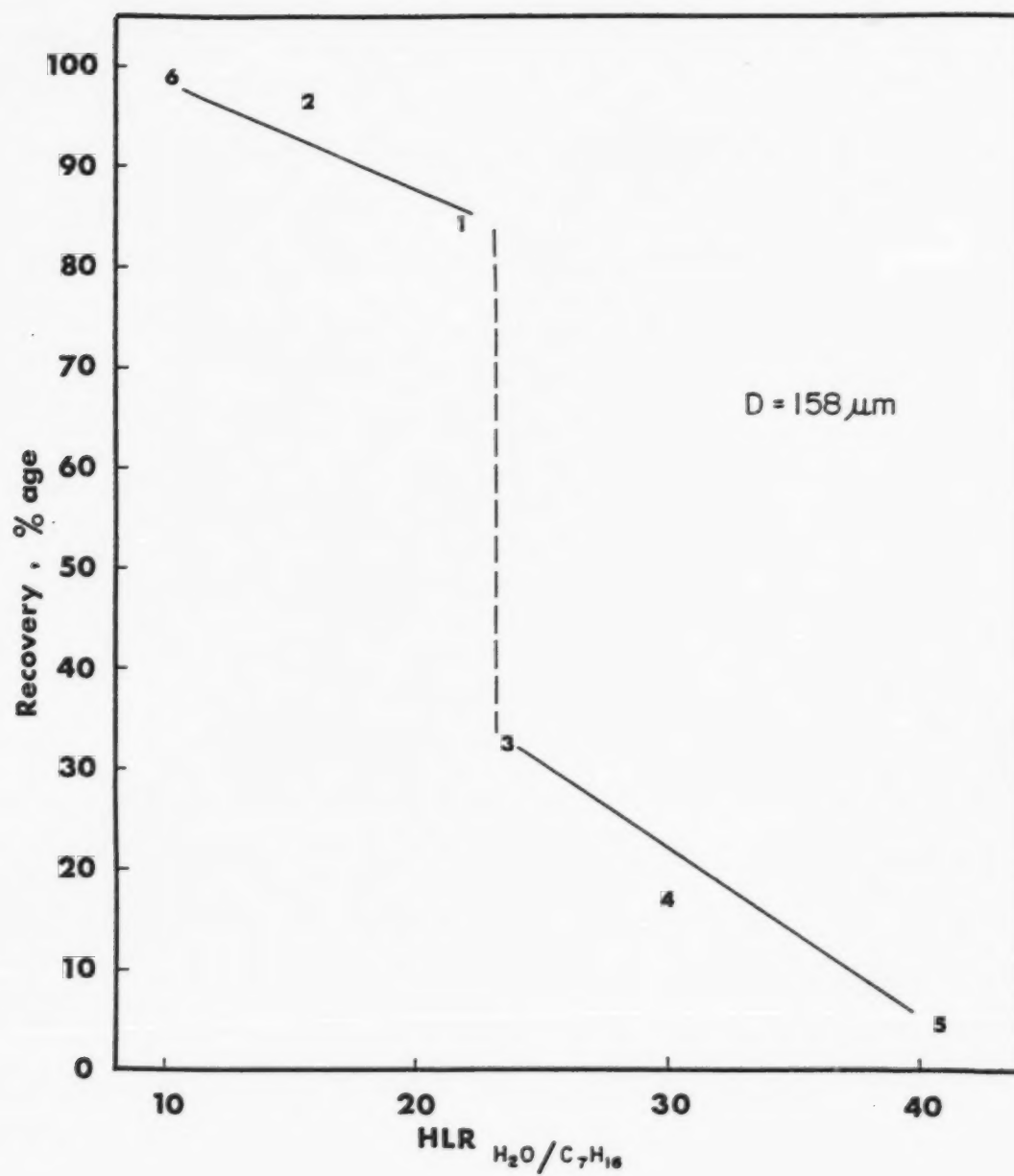


Figure 96 Relationship Between the Surface Characteristics of Coal and Its Recovery (HLR Evaluated Using Water and n-Heptane)

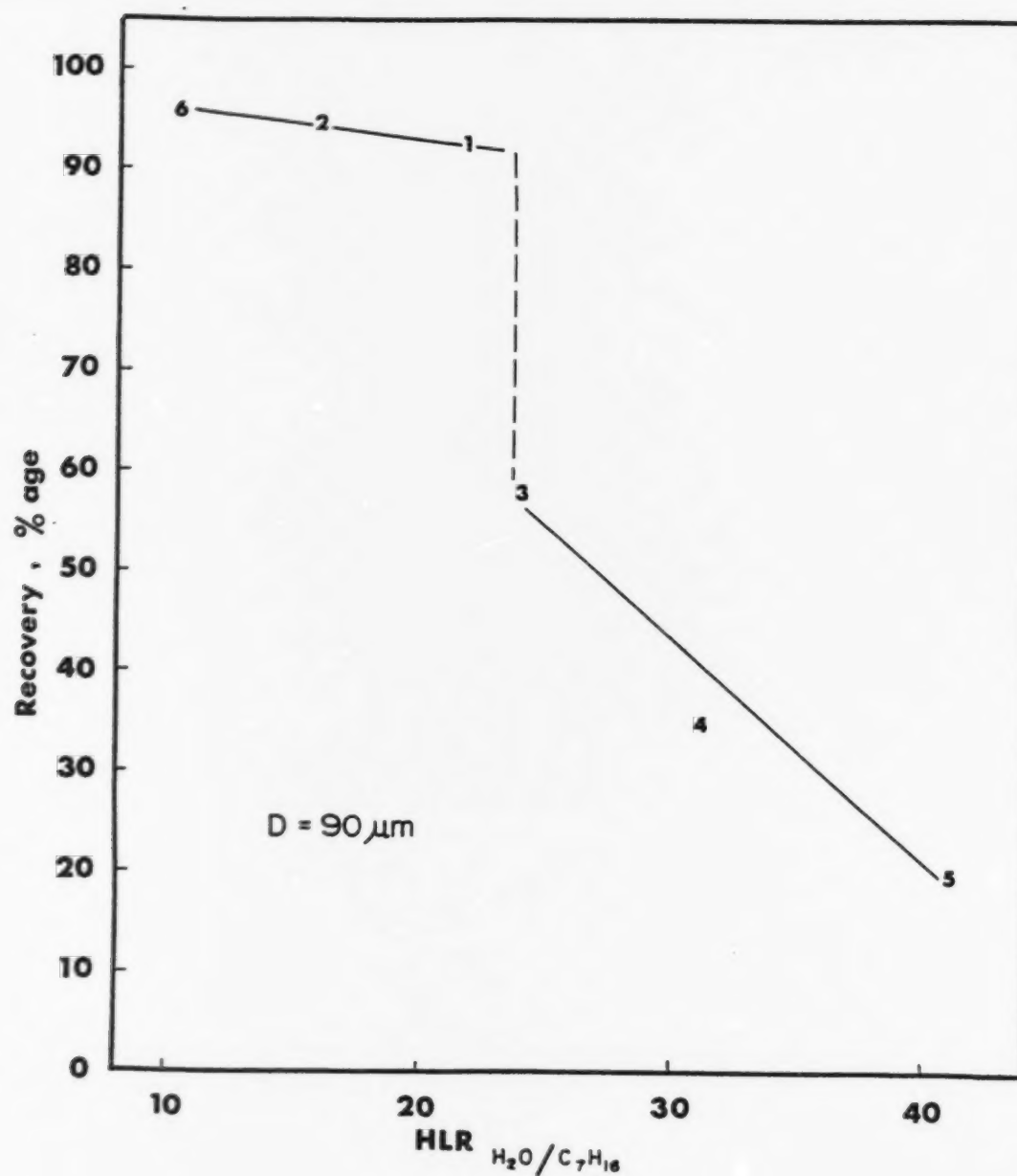


Figure 97 Relationship Between the Surface Characteristics of Coal and Its Recovery (HLR Evaluated Using Methanol and n-Heptane)

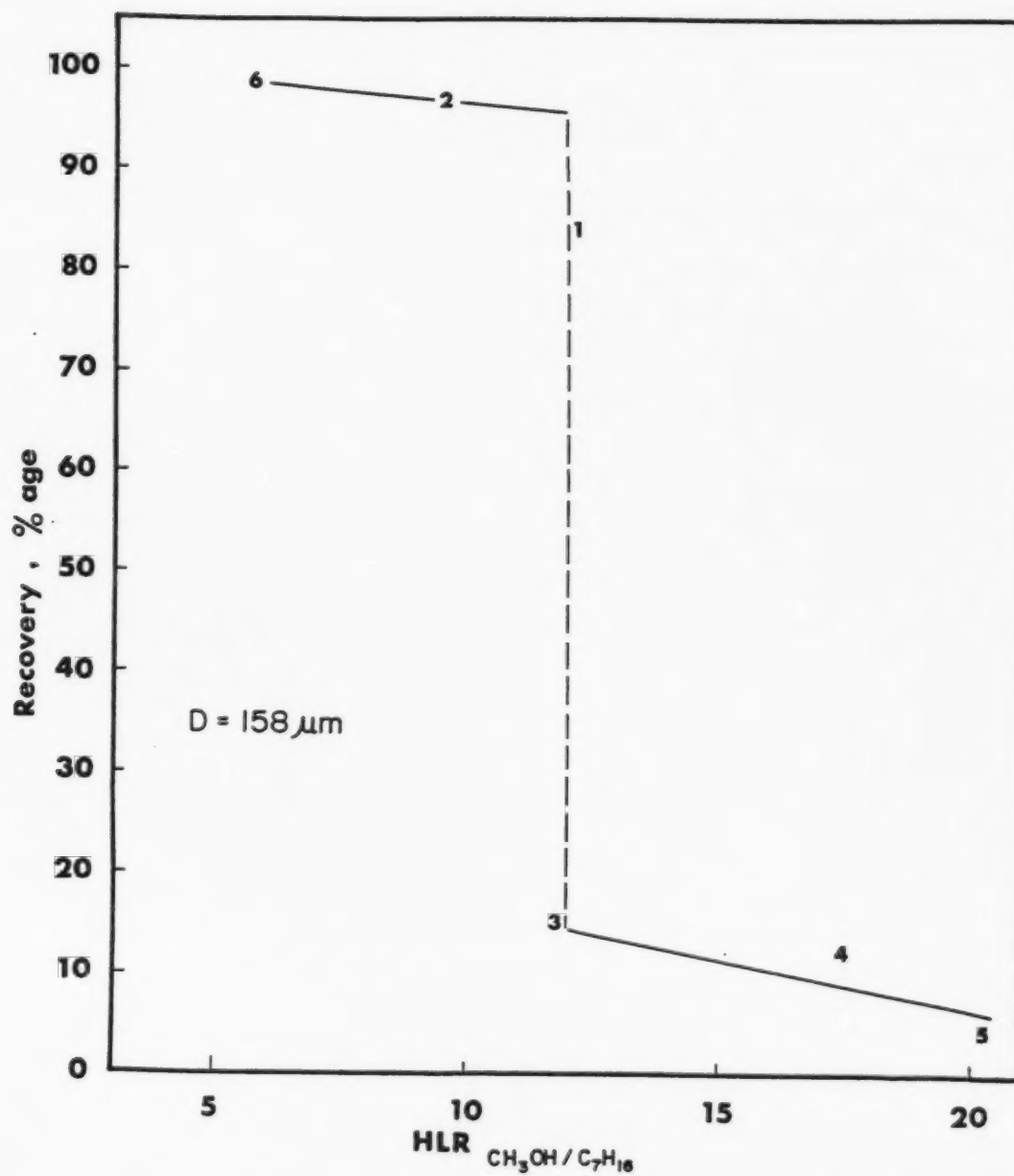


Figure 98 Relationship Between the Surface Characteristics of Coal and Its Recovery (HLR Evaluated Using Methanol and n-Heptane)

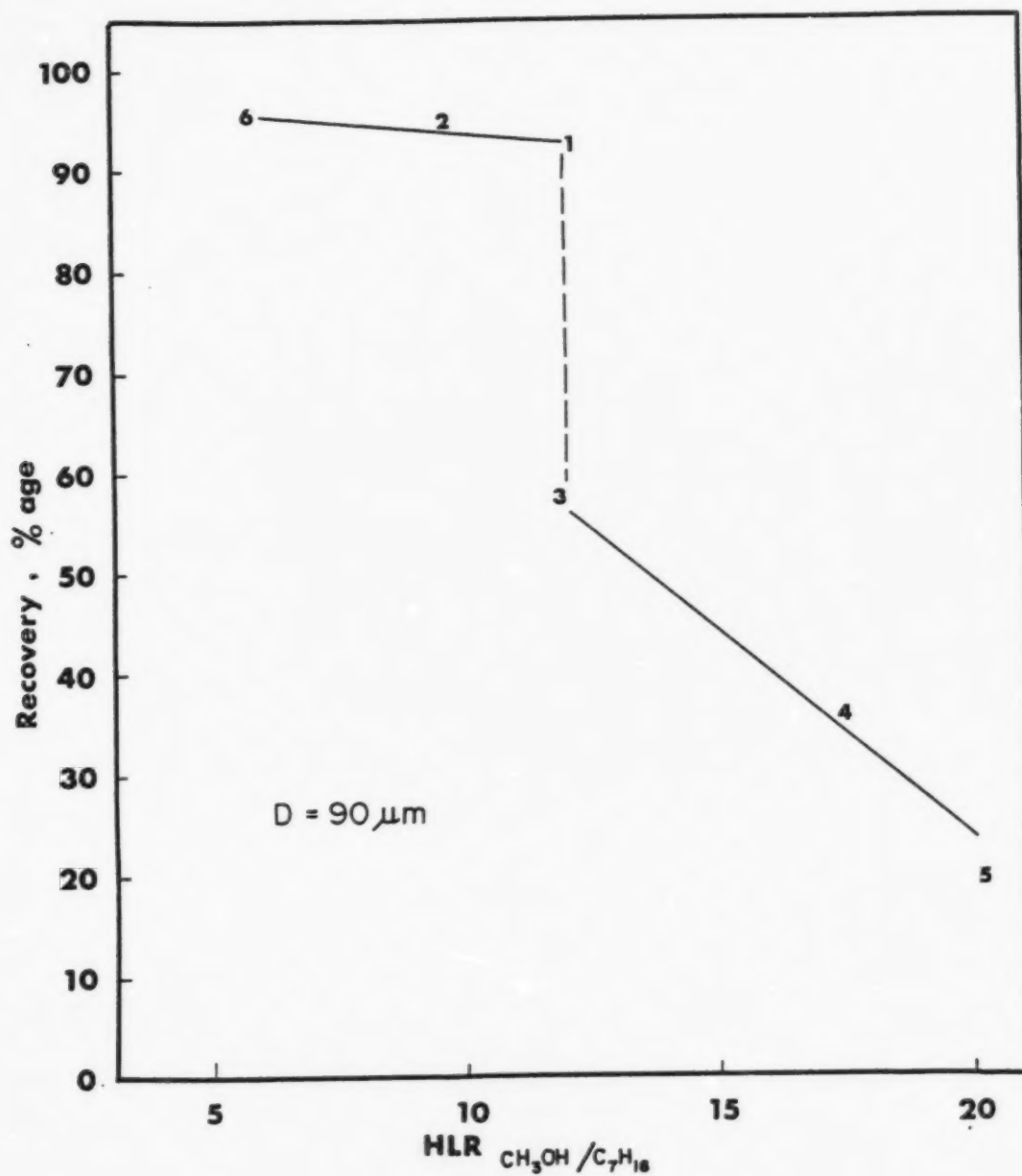


Figure 99 Relationship Between the Surface Characteristics of Coal and Its Recovery (HLR Evaluated Using Methanol and n-Heptane)

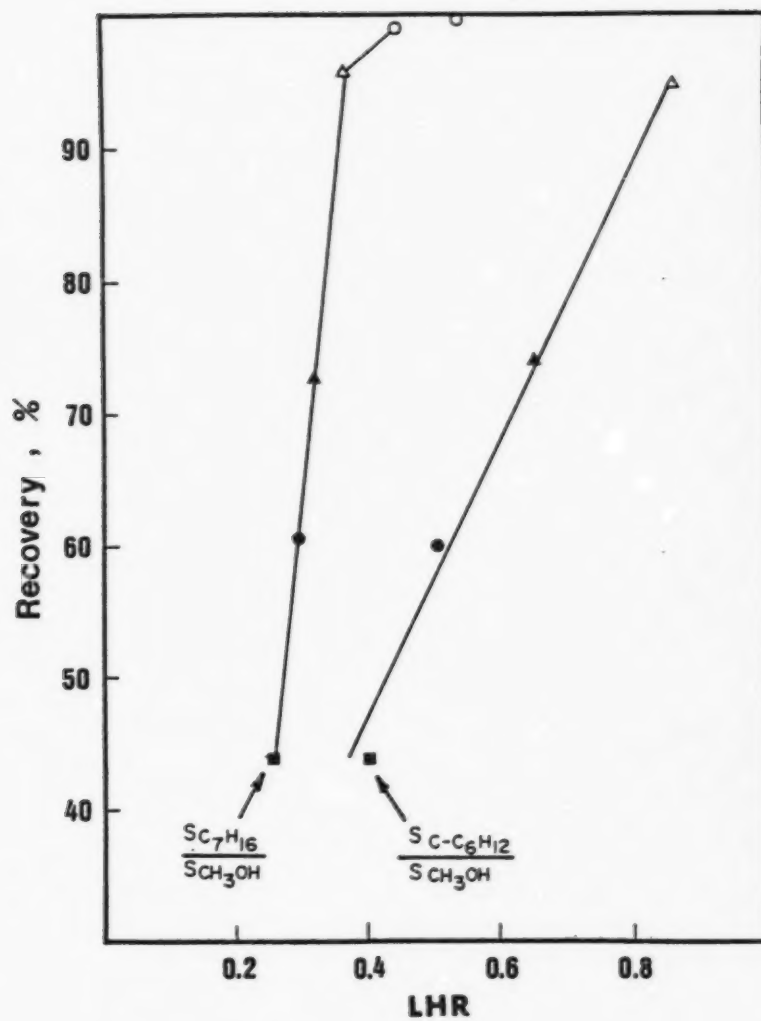


Figure 100 Relationship Between the Surface Characteristics of Maritime Coals and Flotation Recovery.

III.11 Effect of Surface Conditioning On Coal Flotability

Several additives have been proposed to improve the flotability of difficult-to-float coals. Most common of these are the collector oils (kerosene, fuel oil, etc.) as well as various polar surface conditioners. Use of such reagents relies on their ability to be adsorbed on, or attached to, the surface of the coal with the resultant increase in its effective hydrophobicity. Additives type and dosage, as well as the hydrodynamic parameters and duration of the surface conditioning stage play an important role in the effectiveness of this approach.

The following reagents were tested with respect to their ability to improve the flotability of coal:

- Alchem 8E34
- DOW M210
- Ethyl Acetate
- Fuel Oil No. 2
- Heptanol
- Hexadecylpyridinium Bromide HPB
- Kerosene
- Methyl Isobutyl Carbinol MIBC
- pH

Because of its significance the effect of conditioning time and collector emulsification was also investigated and the results obtained are listed in Tables 32-35.

TABLE 32 Effect of Surface Conditioning on the Flotability of Maritime Coal

Test No.	Coal	Particle Size	pH	Conditioner	Collector	% Recovery
1	Prince (oxidized for 120 hours)	-70 +100	5.7	--	--	23 ± 1
2		"	"	20 ppm HPB	--	24.6 ± 0.2
3		"	"	--	1 Kg/T Kerosene	44 ± 0.2
4		"	"	20 ppm HPB	1 Kg/T Kerosene	44 ± 0.3
5		"	6.8	--	--	28.5 ± 0.3
6		"	"	5 ppm HPB	--	34 ± 0.5
7		"	"	52 ppm HPB	--	35 ± 0.5
8		"	9.8	--	--	40 ± 0.3
9		"	10.0	45 ppm HPB	--	55.5 ± 0.5
10		"	10.1	150 ppm HPB	--	67 ± 1
11	Prince	-28 +35	7.7	--	--	96.8 ± 0.2
12		"	7.0	150 ppm HPB	--	96.5 ± 0.3
13		"	5.7	--	--	15.8 ± 0.5
14		"	"	8 ppm HPB	--	14.0 ± 0.4
15		"	"	1000 ppm MIBC		92.8 ± 0.4
16		"	"	1000 ppm MIBC 8 ppm HPB		77.6

10 ppm MIBC, 0.01 M NaCl, 24 hrs
conditioning time, Siwek Flotation Cell

TABLE 33 Effect of Surface Conditioning on the Flotability of Western Coals*

Test No.	Coal Tested	Particle Size	pH	Conditioner	Conditioning Time	Collector	% Recovery	Remarks
17	EMR 1	-140 +200	7.2	--	5 min	--	95.6 ± 1	
18	"	"	7.2	--	"	1 Kg/T (Kerosene)	98.8 ± 0.1	
19	"	"	7.3	--	"	0.2 Kg/T (M210) 0.8 Kg/T (Kerosene)	97.8 ± 0.1	
20	"	"	6.7	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	99.0	
21	"	"	6.5	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	98.2 ± 0.1	
22	"	"	6.7	0.1 Kg/T (Heptanol)	"	1 Kg/T (Kerosene)	99.0 ± 0.1	
23	EMR 2	"	8.0	--	"	--	98.6 ± 0.4	
24	"	"	7.9	--	"	1 Kg/T (Kerosene)	99.7	
25	EMR 3	"	8.4	--	"	--	64 ± 2	
26	"	"	7.6	--	"	1 Kg/T (Kerosene)	93 ± 2	
27	"	"	7.7	--	"	0.2 Kg/T (M210) 0.8 Kg/T (Kerosene)	83 ± 2	
28	"	"	8.0	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	84.1 ± 0.6	
29	"	"	8.1	0.2 Kg/T (M210)	"	--	86 ± 2	
30	"	"	7.8	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	78 ± 1	
31	"	"	7.8	0.1 Kg/T (Heptanol)	"	1 Kg/T (Kerosene)	81 ± 3	
32	"	"	8.4	--	25 min	--	58 ± 3	
33	"	"	7.7	--	"	1 Kg/T (Kerosene)	95.5 ± 1	
34	"	"	7.7	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	90 ± 4	
35	"	"	7.8	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	81 ± 2	Good emulsification of M210, but not for Kerosene.

Test No.	Coal Tested	Particle Size	pH	Conditioner	Conditioning Time	Collector	% Recovery	Remarks
36	"	"	7.9	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	92 ± 2	Good emulsification for both M210 and Kerosene.
37	"	"		0.5 Kg/T Ethyl Acetate	"	1 Kg/T (Kerosene)	77 ± 2	
38	"	"		0.1 Kg/T Alchem RE 34	"	1 Kg/T (Kerosene)	76 ± 3	
39	EMR 4	"	7.2	--	5 min	--	38 ± 1	
40	"	"	7.3	--	"	1 Kg/T (Kerosene)	88 ± 2	
41	"	"	7.4	--	"	0.2 Kg/T (M210) 0.8 Kg/T (Kerosene)	68 ± 3	
42	"	"	7.3	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	77 ± 4	
43	"	"	7.2	0.2 Kg/T (M210)	"	--	73 ± 6	
44	"	"	7.2	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	69 ± 4	
45	"	"	7.2	0.1 Kg/T (Heptanol)	"	1 Kg/T (Kerosene)	61 ± 6	
46	"	"	7.3	--	25 min	--	41 ± 2	
47	"	"	7.3	--	"	1 Kg/T (Kerosene)	82 ± 1	
48	"	"	7.1	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	83 ± 2	
49	"	"	7.2	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	80.6 ± 0.2	Good emulsification of M210 but not for Kerosene.
50	"	"	7.3	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	84 ± 1	Good emulsification for both M210 and Kerosene.
51	"	"	7.2	0.05 Kg/T Ethyl Acetate	"	1 Kg/T (Kerosene)	55 ± 3	
52	"	"	7.3	0.1 Kg/T Alchem BE 34	"	1 Kg/T (Kerosene)	53 ± 2	
53	EMR 5	"	6.3	--	5 min	--	22 ± 2	
54	"	"	7.2	--	"	1 Kg/T (Kerosene)	32 ± 5	
55	"	"	7.4	--	"	0.2 Kg/T (M210) 0.8 Kg/T (Kerosene)	42 ± 5	

Test No.	Coal Tested	Particle Size	pH	Conditioner	Conditioning Time	Collector	% Recovery	Remarks
56	"	"	6.7	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	33 ± 1	
57	"	"	6.5	0.2 Kg/T (M210)	"	--	40 ± 3	
58	"	"	6.7	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	27 ± 2	
59	"	"	6.9	0.1 Kg/T (Heptanol)	"	1 Kg/T (Kerosene)	25 ± 1	
60	EMR 5 (a more hydrophilic sample)	"	6.7	--	25 min	--	14 ± 2	
61	"	"	6.8	--	"	1 Kg/T (Kerosene)	16 ± 1	
62	"	"	6.4	--	"	0.05 Kg/T (M210) 0.95 Kg/T (Kerosene)	22.5 ± 0.6	
63	"	"	6.2	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	35 ± 2	Good emulsification of M210 but not for Kerosene.
64	"	"	6.0	0.1 Kg/T (M210)	"	1 Kg/T (Kerosene)	47 ± 2	Good emulsification for both M210 and Kerosene.
65	"	"	6.2	0.05 Kg/T Ethyl Acetate	"	1 Kg/T (Kerosene)	38 ± 2	
66	"	"	6.2	0.1 Kg/T Alchem 8E34	"	1 Kg/T (Kerosene)	45 ± 2	
67	EMR 6	"	7.2	--	5 min	--	98 ± 1	
68	"	"	7.8	--	"	1 Kg/T (Kerosene)	99 ± 0.5	

10 ppm MIBC, 0.01 M NaCl, Siwek flotation cell

**TABLE 34 effect of Emulsification Extent and Surface Conditioning
On the Flotation Yield of Western Coals***

I 1 Kg Kerosene/Tonne Coal (Emulsified at pH 10)

Run			% Recovery
69	EMR 3		95.5 $\pm$ 0.5
70	EMR 4		82 $\pm$ 0.4
71	EMR 5		20.5 $\pm$ 1

II 1 Kg of (90% Kerosene, 10% M210)/Tonne Coal (Emulsified at pH 10)

Run			% Recovery
72	EMR 3		94.5 $\pm$ 0.5
73	EMR 4		86 $\pm$ 0.5
74	EMR 5		36 $\pm$ 1

III 1 Kg of (90% Kerosene, 10% M210)/Tonne Coal (Emulsified at pH 7)

Run			
75	EMR 3		81 $\pm$ 0.5
76	EMR 4		81 $\pm$ 1
77	EMR 5		35 $\pm$ 2

- +, 10 ppm MIBC, 0.01 M NaCl, microflotation cell

**TABLE 35 Effect of Collector Emulsification on
Flotation Yield of Maritime Coal***

I 1 Kg No. 2 fuel Oil/Tonne Coal

	% Recovery After	
	1 min.	10 min.
a) Surface addition	18 $\pm$ 3	28 $\pm$ 1
b) Surface stirring	35 $\pm$ 2	44 $\pm$ 1
c) Pre-emulsified	41 $\pm$ 1	45 $\pm$ 0.5

II 0.1 Kg No. 2 Fuel Oil/Tonne Coal

	% Recovery After	
	1 min.	10 min.
a) Surface addition	14 $\pm$ 2	26 $\pm$ 1
b) Surface stirring	26 $\pm$ 1	38 $\pm$ 0.5
c) Pre-emulsified	30 $\pm$ 0.3	42.5 $\pm$ 0.5

-30 mesh Prince coal (PRO02), 10 ppm MIBC, 0.01 M NaCl ISO flotation cell

As can be seen from Table 32 variation in the pH value can have a significant effect on coal recovery with the impact being most pronounced for larger particles. This can be attributed to the important role of H^+ and OH^- in determining the contact angle between bubbles and coal particles (86). The fact that larger particles are more susceptible to variations in pH can be attributed to the interaction between the hydrodynamic rupture forces and the attachment forces between bubbles and particles.

Because of the sensitivity of HPB distribution coefficient to variations in pH values, and the need for its molecules to adsorb on the hydrophillic active sites present on the surface of the coal in order to enhance its effective hydrophobicity, no significant improvement in recovery was observed at low pH values (Runs 1 vs 2, 3 vs 4, 11 vs 12 and 13 vs 14) whereas it was quite effective at higher pH values (Runs 5, 6, 7 vs 8, 9, 10). On the other hand, MIBC is a good surface conditioner at low pH values (Runs 15, 16) and can thus play a dual role in coal flotation. It can thus enhance the hydrophobicity of coal surfaces by means of its adsorption on active hydrophillic sites (with its hydrophobic tail being oriented towards the aqueous phase) as well as improving gas/liquid contacting in both the pulp and froth phases. Preliminary indications are that the presence of HPB reduces the effectiveness of MIBC as a surface conditioner (Run 16) and suggest that synergistic interactions between additives must be closely scrutinized.

The use of Kerosene was found to be quite effective in improving the recovery of coals with unfavourable flotation characteristics (Runs 3, 4).

Pretreatment with HPB prior to the use of Kerosene was not found to be effective because of the low pH value at which the test was conducted (Run 4).

Use of Kerosene in conjunction with coals of relatively good flotation response (Runs 17-22) was found to result in slight improvement which is not significantly improved by surface conditioning. Substitution of a significant fraction of Kerosene by M210 resulted in a slight reduction in collection efficiency (runs 18 vs 19). A similar situation was observed to exist in the case of other coals with similarly good flotation characteristics (e.g. coals EMR 2 and EMR 6) whereas the situation is completely different with coals of lower flotability. It should be cautioned, however, that these conclusions are based on the experience gained with relatively small particles and that the trends may, therefore, be somewhat different in the case of larger particles.

In the case of EMR 3 sample use of Kerosene was found to improve flotation recovery by almost 30% (Runs 25 vs 26) and partial replacement of the Kerosene by M210 was found to reduce recoveries, most probably because of greater difficulties in emulsifying the mixtures. Use of M210 alone was found to improve recoveries by more than 20% (Run 29) but preconditioning the coal with either M210 or Heptanol was found to reduce the recovery (Runs 30, 31). No plausible explanation can be presented but this phenomenon persisted when Ethyl Acetate and Alchem 8E34 were used (Runs 37 and 38) as well as at longer conditioning times (Runs 34-36). The tendency of coal surfaces to hydrate upon prolonged contact with water is evidenced by the reduction in flotation

recoveries observed when conditioning time was increased from 5 to 25 minutes (Runs 25 vs 32).

The importance of proper contacting between the immiscible conditioner and collector phases and coal particles is highlighted by the impact of reagent pre-emulsification on the recovery of coal. Thus for example, inadequate emulsification of Kerosene was found to result in the loss of about 14% in spite of the presence of a surface conditioner (Runs 33 vs 35). Proper emulsification of the conditioner M210 was found to enhance coal recovery by 3-11% (Runs 30 vs 35, 44 vs 49 and 58 vs 63) whereas proper emulsification of both conditioner and collector was found to improve recoveries by 14-20% (runs 30 vs 36, 44 vs 50 and 58 vs 64). The importance of proper dispersion of insoluble flotation reagents is further confirmed by the data shown in Table 34 where it was qualitatively observed that better dispersion of the reagents was obtained by mechanically emulsifying them at high pH values.

These observations are in line with those of Aplan (97) as well as Barcal and Dedek (98) but there is however, no quantitative relationship between the extent of oil dispersion and coal beneficiation. A research program addressing this deficiency will shortly be undertaken at our laboratories. Preliminary indications (Table 35) suggest that the influence of oil emulsification is strongly a function of oil dosage and retention time in the flotation cells with more than 100% improvement being obtained at small retention times.

Because of the lower hydrophobicity of sample EMR 4, relative to EMR 3, the recoveries achieved under identical conditions are 15-30% lower. This differential is, however, substantially reduced by proper application of effective conditioners (Runs 49 and 50 vs 35 and 36), thereby confirming the substantial economic benefits that can be gained from the adoption of appropriate processing technology. A similar but somewhat stronger tendency was observed in conjunction with sample EMR 5 (Runs 53-66).

The significance of adequate conditioning time becomes more pronounced the greater the hydrophilicity of the coal. Thus, by increasing the conditioning time from 5 to 25 minutes, coal recoveries were increased by 14, 15 and 20% for EMR samples No. 3, 4 and 5 respectively. Coal EMR 5 differs from all other samples in the relatively high conditioning effectiveness exhibited by ethyl acetate and Alchem 8E34 (Runs 65 and 66 vs 64). A large part of the difference between Runs 53-59 and Runs 60-66 is thought to result from the longer conditioning time encountered in the latter; however, it is suspected that the use of a new coal sample (with higher inherent moisture content) could have resulted in the latter runs being conducted on a more hydrophilic sample.

A good indication of the relative significance of good dispersion of the reagents versus the benefits gained from the use of surface conditioners can be obtained by examining the data presented in Table 34. Thus, for relatively hydrophobic coals proper emulsification of the collector plays a more significant role (Runs 69 and 72 vs 75) whereas with highly hydrophilic coals the

use of proper surface conditioner plays a more significant role than the extent to which the collector is dispersed (Runs 74 and 77 vs 71). The data shown in Table 35 show the great significance of collector dispersion in the case of a relatively hydrophobic coal, but these results cannot be directly compared with those of Table 33 because of the difference in particle size as well as the hydrodynamic conditions in the ISO cell.

IV CONCLUSIONS

1. The surface characteristics of coal play an important role in determining the effectiveness of its beneficiation by flotation. The following methods for characterizing its surface properties were tested:
 - A) Wetting time.
 - B) Contact angle on a compacted pellet.
 - C) Capillary pressure during liquid imbibition.
 - D) Dynamic penetration of liquid through a packed bed of powder.
 - E) Minimum pressure needed for the formation of a bubble.
 - F) Heat of wetting.
 - G) Vapour adsorption.
 - H) Drop drainage time.
2. The sensitivity of the various techniques to systematic variations in the surface characteristics of coal can be ranked as follows:
 $G > F > H > D > A > C > E$.
3. Under the conditions investigated, measurement of the contact angle on a compacted pellet was found to be unsatisfactory.
4. With the exception of A and E, all techniques were found to exhibit similar normalized tendencies. The discrepancy observed in the case of technique E could stem from its reliance on receding contact-angle instead of the advancing contact-angle as is the case with all other tests.

5. A strong correlation exists between the reproducibility of any particular test and the magnitude of the measured parameter. The larger the value of the measured parameter the better is the test's reproducibility, and vice versa. Most wettability measuring techniques have a normalized variance of less than 5% and can be further improved by proper selection of wetting solutions.
6. Based on a comparative evaluation of the cost and labour requirements for various wettability measuring techniques (Table 30), it was not possible to recommend any particular method. The advantages of simple and inexpensive techniques have to be balanced against their high labour demands. Furthermore, although simple tests yield good indication of the overall hydrophobicity of the surface the information they generate is rather limited when compared to that generated by more sophisticated approaches.
7. Prolonged exposure of coals to an oxidizing environment was found to result in the gradual loss of their hydrophobic nature until a new equilibrium state is reached. In the case of the Maritime coals investigated, this was observed to occur after about 120 hours of exposure to oxygen at 100°C.

The energy of interaction between polar molecules and the active sites present at the new equilibrium condition is about twice that for active sites present in natural environment (Figure 49).

8. The susceptibility of coal to oxidation appears to be strongly related to its pore structure with more porous coals being more prone to weathering.
9. The coal samples investigated can be classified according to the descending level of natural hydrophobicity.

Maritime Coals:

Devco > Minto > Westville > Evans > Prince

Western Coals:

6 > 2 > 1 > 3 > 4 > 5

10. The pore size distribution of Western coal samples (Fig. 79) suggests a progressive reduction in the median pore size with increasing hydrophobicity.
11. The pore structure and surface area of coal as determined by adsorption technique, was found to be strongly dependent on the type of adsorbate used, the nature of coal as well as the conditions at which it was exposed to oxidation. The non systematic variations and discrepancies can be reconciled by taking the heterogeneity of the coal's surface into consideration. The surface of the coal is, therefore, considered to have a large number of active sites that interact with the adsorbate. The energy of interaction with any particular adsorbate is described by a site -energy distribution function which is dependent on the nature of the active site, that of the adsorbate as well as the temperature and

pressure at which adsorption takes place. The overall surface characteristics may thus be approximated by the ratio of the hydrophillic to lyophillic active sites (HLR).

12. Flotation recoveries of relatively small particle sizes are not strongly influenced by the surface characteristics of coal. This can be explained by the fact that the forces causing the rupture of particle/bubble aggregates are inversely proportional to particle diameter; hence, the overall flotation rate is determined by the bubble-particle collision step. On the other hand, flotability of large coal particles is strongly influenced by its surface characteristics since under these conditions the probability of bubble/particle detachment plays the controlling role.
13. Coal recovery was found to correlate rather poorly with its intrinsic properties (C, O₂ and moisture) with the scatter increasing with particle size. Better success was achieved when recoveries were correlated using surface-characteristics parameters (e.g. minimum bubble pressure, heat of wetting etc.).
14. The six Western coal samples can be classified into two distinct groups with respect to the influence surface characteristics have on flotation recovery. The "wettability" at which the transition from one group to the other takes place is expected to be dictated by the hydrodynamic conditions within the cell. The recovery of coal particles more hydrophillic than this critical value is strongly affected by particle size

with the surface characteristics playing a progressively larger role the smaller particles are. On the other hand, the recovery of particles which are more hydrophobic than the critical value is only marginally affected by particle size and becomes progressively insensitive to variations in surface characteristics with decreasing particle size.

15. The overall wettability of a heterogenous coal surface may be characterized by the ratio of the hydrophillic to the oleophillic sites present on the surface of the coal. Using such an indicator, good correlation with recovery was obtained for both Western and Maritime coals.
16. The use of hydrocarbon collectors (Kerosene or fuel oil) was found to be most effective in improving the recovery of coals which exhibit relatively good hydrophobicity, but is less effective in the case of more hydrophillic coals. However, by properly conditioning the surface of the latter it tends to be more responsive to the use of collectors.
17. The effectiveness of using hydrocarbon collectors can be substantially improved by properly emulsifying it prior to its introduction to the conditioning of flotation stage.
18. Amongst the reagents tested MIBC, HPB and Dow M210 were found to be most effective in improving the hydrophobicity of coal. The impact of such treatment is most significant the larger the particles are and the more hydrophillic is the coal.

19. Because of the sensitivity of HPB distribution coefficient to slight variations in pH value, its utilization for conditioning coal surfaces is limited to higher pH values.
20. Since surface conditioning proceeds through an adsorption process, the period for which the coal is allowed to contact the reagents plays an important role. This is particularly important in the case of highly hydrophillic coals (e.g. subbituminous coals).
21. The above-mentioned findings suggest that upon collision with coal particles hydrocarbon collectors modify the surface characteristics by spreading and coverage of moderately hydrophobic sites. Pre-emulsification of the oil enhances this process by enabling the oil to cover a larger surface area. However, for this process to proceed it is necessary that the coal's surface exhibit a minimum degree of hydrophobicity, which may be lacking in the case of low-rank and severely weathered coals. Use of appropriate surface conditioners may thus enable the coal's surface to make better use of collectors by providing the minimum hydrophobicity needed for collision and spreading.

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